

## **0.0 INTRODUCTION**

The quality assurance policy of the U.S. Environmental Protection Agency (EPA) requires every environmental data collection activity to have a written and approved quality assurance project plan (QAPjP).

This requirement applies to all environmental monitoring and measurement efforts authorized or supported by EPA through regulations, grants, contracts, or other formal means. The purpose of this QAPjP is to specify the policies, organization, objectives, and the quality evaluation (QE) and quality control (QC) activities needed to achieve the data quality objectives of the Lake Michigan Mass Balance Study. These specifications are used to control and assess measurement uncertainties that may enter the system at various phases of the project, e.g., during sampling, preparation/staging, and analysis.

The GLNPO Surveillance and Research Staff (SRS) are committed to fulfilling the objectives of the Lake Michigan Mass Balance Study. Environmental managers, including the GLNPO Director will make decisions based upon the interpretive results of this program. By way of signature approval, the SRS have agreed to the policy and guidance developed in the QAPjP. All organizations cooperating on the Lake Michigan Mass Balance Surveys will adhere to the guidance and policy within the QAPjP. Any agency or group currently cooperating on the Lake Michigan Mass Balance Surveys, or considering cooperating, will receive a copy of the QAPjP.

GLNPO utilizes a four-tiered project category approach to its QA Program in order to effectively focus QA. This approach was developed by the U.S. EPA, Risk Reduction Engineering Laboratory, Cincinnati, Ohio (EPA/600/9-89/087). The SRS has identified the Lake Michigan Mass Balance Surveys as a Category II QAPjP. A Category II QAPjP is defined as:

*Projects producing results that compliment other inputs. These projects are of sufficient scope and substance that their results could be combined with the results of other projects of similar scope to produce narratives that would be used for rule making, regulation making, or policy making. In addition, projects that do not fit this pattern, but have high visibility, would also be included in this category.*

Guidelines for this category can be found in EPA document 600/8-91/004 and is available to GLNPO staff.

The QAPjP is meant to be a dynamic document, changing as more information is acquired, or objectives change. The QAPjP will be revised to reflect these changes and will update the approval page as major modifications occur.

## **1.0 PROJECT DESCRIPTION**

### **1.1 Relevance of Lake Michigan Mass Balance Surveys**

The general requirements for data to support development of the mass balance models requires monitoring surveys to measure the spatial gradients and variability of the various contaminant concentrations. Seasonal sampling surveys will be conducted to monitor temporal as well as spatial variability in water column concentrations of parameters needed for the mass balance models. Such data will serve to confirm partitioning and phytoplankton bioconcentration predictions. Sediment sampling will be conducted to measure the inventory of toxics in the surficial mixed layer throughout the lake, as well as the fine-scale vertical distribution of toxics in depositional sediment cores. Biota collections will be targeted to sample the variation of toxics concentrations both with season and location.

### **1.2 Purpose**

The purpose of the Lake Michigan Mass Balance Surveys is to collect biological, chemical and physical water quality data for use in the Lake Michigan Mass Balance Study model. The objectives of this Study and model are:

- to identify relative loading rates of critical pollutants from major tributaries to the Lake Michigan basin in order to better target future load reduction efforts:

- to evaluate relative loading rates by media (tributaries, atmospheric deposition, contaminated sediments) in order to better target future load reduction efforts and to establish a baseline loading estimate to gauge future progress:

- to develop the predictive ability to determine the environmental benefits of specific load reduction scenarios for toxic substances and the time required to realize those benefits. This includes evaluation of benefits of load reductions from existing environmental statutes and regulations as required under Section 112(m) of the CAA, and Section 303 of the Clean Water Act (CWA), and;

- to improve our understanding of key environmental processes which govern the cycling and bioavailability of contaminants within relatively closed ecosystems.

### **1.3 Survey Outline**

Table 1-1 pertains to a two year program, which includes spring, summer fall and winter surveys. Each survey is important for determining seasonal values for contaminants in the water column and lower food chain, and for determining other chemical and biological information necessary to support the modeling effort.

**Table 1-1 GLNPO LAKE MICHIGAN MASS BALANCE SURVEY Plan**

Lake Michigan Mass Balance Study	April, 1994 - November 1995
Survey	April, June-July, August, October
Region	Lake Michigan
Vessel	R/V Lake Guardian
Master	Captain R. Ingram
Agency	United States Environmental Protection Agency
Chief Scientist	Dr. G.J. Warren
Chief Chemist	Mr. D.A. Anderson
Chief Inorganic Chemist	Mr. M.F. Palmer
Chief Biologist	Dr. P.E. Bertram
Ship Project Officer	Mr. D.C. Rockwell

#### 1.4 Parameters of Interest

Table 1-2 summarizes the parameters to be measured in the LAKE MICHIGAN MASS BALANCE SURVEY. The parameters will be divided into three main categories: 1) nutrients, 2) physical and 3) biological. Throughout the QAPjP these categories will be used as reference to the parameters contained within them.

**Table 1-2. List of Parameters and Corresponding Sampling & Analysis Techniques for the LAKE MICHIGAN MASS BALANCE SURVEY.**

Parameter	Sampling Instrument	Sampling Method	Analysis Technique	Analysis Method	Units	Method Detection Limit/Units
<b>Nutrients</b>						
Total Kjeldahl N	Rosette	App B Sec. 1	Autocolorimetric	App C. Sec.		0.05
Nitrate + Nitrite N	"	"	"	App C. Sec.	mg/L	
Total P	"	"	"	App C. Sec.		0.03
Total Dissolved P	"	"	"	App C. Sec.	mg/L	
Chloride	"	"	"	App C. Sec.		0.001
Reactive Si	"	"	"	App C. Sec.	mg/L	
Particulate Organic C	"	"				0.001
Dissolved Organic C	"	"				
					mg/L	0.2
					mg/L	0.015
					mg/L	
<b>Physical</b>						
Aesthetics	Observation	NA	NA	NA		
Temperature						
Air	Thermistor		NA	NA	0.5°C	

Water	EBT/Therm.		"	"	0.1 °C
Wind Speed	Met. Station		"	"	1 nautical mph
Wind Direction	Met. Station		"	"	10°
Water Clarity	Secchi		"	"	0.5 meters
Wave Height	Observation		"	"	0.5 ft.
Wave Direction	Observation		"	"	10°
Opt. Transmittance	Sea Bird CTD		SeaTec	"	% transmission
Turbidity	Rosette	App B. Sec. 1	h Trans.		0.01 FTU units
Specific Conductance	Rosette	"	Turbidim		0.9 umho/cm
	Sea Bird CTD		eter	NA	
pH	Rosette	App B. Sec 1	YSI		0.15 pH units
	Sea Bird CTD		Model 35	NA	0.15 pH units
Total Sus. Solids	Rosette	App B. Sec. 1	NA		
Dissolved Oxygen	Rosette	"	Electro		0.007 mg/L
	Sea Bird CTD		metric	NA	
Site Location	Loran		NA		
	C/Radar		Gravime		
			tric		
			Winkler		
			Polarogr		
			aphic		
<b>Biological</b>					
Phytoplankton	Rosette	App B. Sec 1			
Zooplankton	Tow net				
Chlorophyll "a"	Rosette	App B. Sec 1			
Phaeophytin "a"	Rosette				
Mysis relicta	Tow net or sled	"			
Diporeia spp.	Sled				

### 1.5. Project Schedule

The R/V Lake Guardian is scheduled for 21 to 31 days of 24-hour operations per survey. Expected sampling time, running time between stations, waste disposal and reprovisioning the ship with fuel and supplies will vary depending on wind, wave, and availability of services when the ship is in port. The survey schedule is persented in Table 1 Appendix A.

The plan is to complete a transit of the track from northern to southern Lake Michigan when possible. Additional days estimated at 25% of sailing days may be needed due to adverse weather conditions.

### 1.6. Vessel

The R/V Lake Guardian is a former offshore oil field supply vessel built by Halter Marine, Moss Point, MS, in 1981. The ship's dimensions are: length - 180', beam - 40', draft - 11', displaced tonnage - 850 tons. Propulsion is twin screws enclosed in Kort nozzles and driven by 1200 hp Caterpillar diesel engines. Cruising speed is 11 knots, range is 6000 miles.

### 1.7. Station Selection

Stations have been selected based upon the objectives of the Lake Michigan Mass Balance Study, which include comprehensive sampling of the Lake, coverage of areas to serve as fish and lower food chain collection sites, and sufficient nearshore area to accomodate model needs.

The locations of the stations in Lake Michigan and Lake Huron (Appendix A, Tables A) are selected from sites within homogeneous areas of the lake as well as nearshore and reef areas.

### 1.8 Site & Depth Selection

Loran C will be used for navigation in locating the stations and in recording drift of the ship while nominally "on station." Radar will be used as the primary system for determining position. In the event that the Loran C and Radar indicate different positions, the Radar will be used to position the vessel and readings from the Loran C will be recorded until the discrepancy can be corrected.

Tables A-6A (Appendix A) give approximate depths for chemical sampling during unstratified (isothermal conditions) and Tables A-6B (Appendix A) give approximate depths for chemical sampling during stratified conditions for Lake Michigan.

For Lake Michigan, unstratified or isothermal sampling depths for stations coincident with the existing monitoring program are: surface (1M), mid-depth, 10 meters from the bottom (B-10) and 2 meters from the bottom (B-2). Samples will be taken at 5 meters and mid depth for stations not coincident with stations from the existing monitoring stations. Samples at master stations will be more frequent through the water column.

During stratified conditions, sampling depths for stations coincident with the existing monitoring program in Lake Michigan are: surface (1M), lower epilimnion 1 meter above the knee (LE), thermocline (T), sub-thermocline chlorophyll maximum, B-10, and B-2. Where water depth is sufficient, samples will also be taken at 100M and 200M. For stations not coincident with stations from the existing monitoring station, samples will be taken at mid epilimnion, sub-thermocline chlorophyll maximum, mid hypolimnion, and nepheloid layer (where existent) - sampling depths will be dependent on initial SeaBird CTD casts to determine location of subthermocline chlorophyll maximum and nepheloid layer.

Phytoplankton will be from a composite of equal volumes from depths of 1, 5, 10, and 20 meters hereafter referred to as the "integrated sample" for all stations. (See discussion on phytoplankton for more details.) When regular sampling depths do not fall within 3 meters of integrated sample depths, samples will be collected at the appropriate depths for use in the composite or "integrated" samples only.

Zooplankton sampling shall be vertical tows from B-2 to the surface, and from 20M to the surface.

*Mysis relicta* samples will be taken at stations in the "biota boxes" as delineated by the National Biological Survey (NBS). Samples will be taken with either whole water column tows with a coarse mesh plankton net, or with a benthic sled.

*Diporeia spp.* samples will be taken at stations in the "biota boxes" as delineated by the NBS, with a benthic sled.

### ***1.9 Dry Run & Shakedown Cruise***

A dry run of the ship laboratory will be performed prior to the ship leaving port. At this time the scientific crew will install the analytical equipment. Contract personnel will demonstrate QC proficiency by analyzing check standards after calibrating the analytical instruments using set standards and demonstrating each analytical system is in control (for out of control situations see section 13).

## **2.0 Project Organization and Responsibility**

### **2.1 Introduction**

Project planning and operation requires close cooperation between EPA Region 5, GLNPO, CRL, and Contractor's personnel. In order to develop and implement the LMMB, communication is essential. Figure 2.1 illustrates the administrative, technical, and QA lines of communication for the parties involved in the LMMB data collection activity. This organizational structure is not meant to hinder communication among participants, but outlines how information should be disseminated among the Survey's administrative, technical, and QA participants. This organizational structure allows for constant feedback between the customers and suppliers which ensures the integrity of data.

### **2.2 LMMB Organization**

The following information describes the responsibilities of the various personnel identified in Figure 2.1.

#### **2.2.1 EPA Contract Officer**

The EPA Contract Officer is the only person authorized to procure supplies and services. The Federal Government is not bound by any commitments made other than this authorized person. Responsibilities of the Contract Officer are:

- Sign contracts
- Obligate funds
- Issue work assignments
- Modify contract terms or conditions
- Terminate contracts
- Accept supplies or services

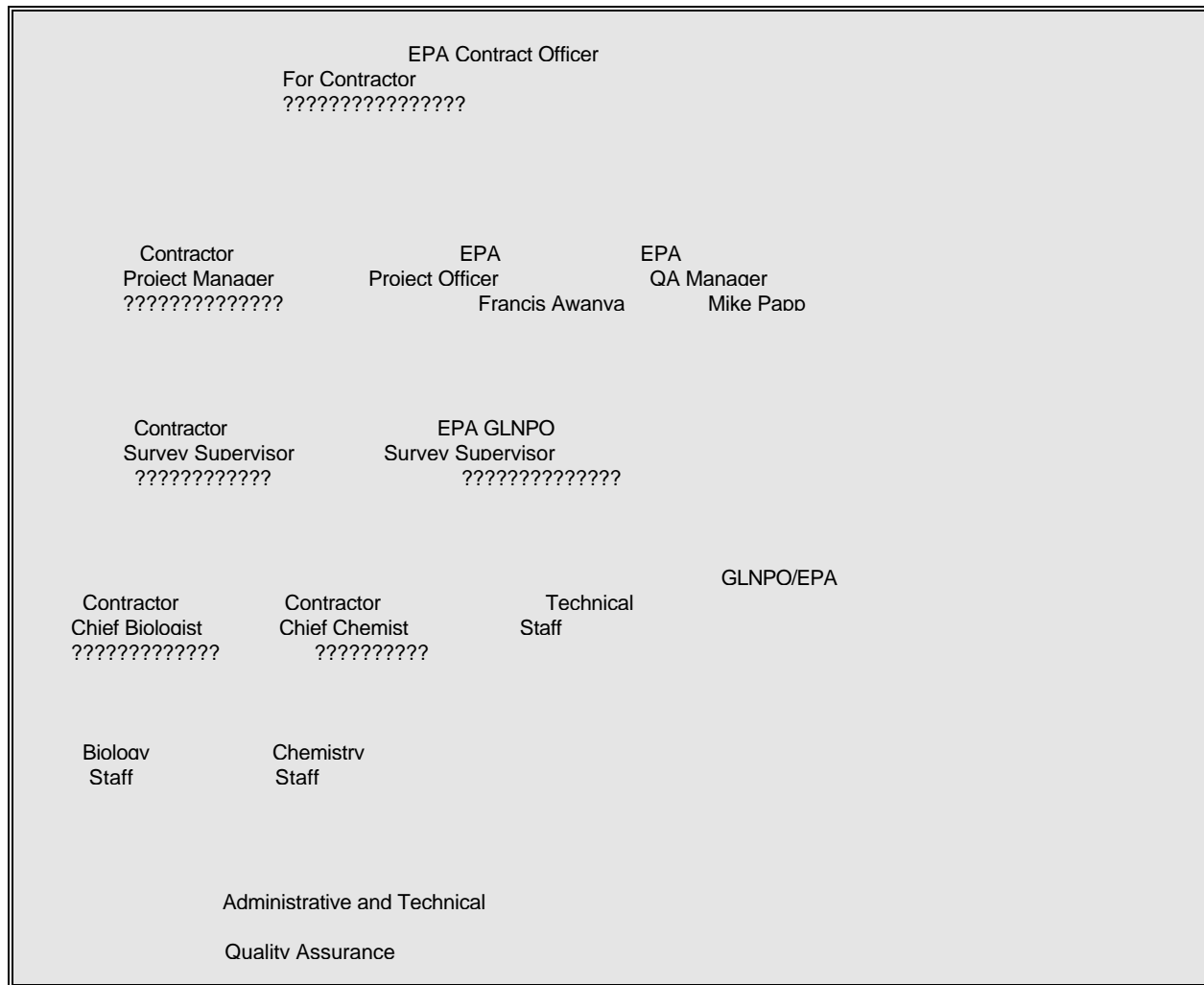
Issuance of work assignments **may** be delegated to the Project Officer **if** this has been stated in the contract. Any communication about contract management, funding, or terms and conditions of the contract will take place, at a minimum, with the Contract Officer, the Contract Project Manager and the EPA Project Officer.

#### **2.2.2 EPA Project Officer**

The Project Officer has overall responsibility to see that the service is provided, but works through the Contract Officer's authority. The Project Officer is appointed by the Contract Officer and formally designated as a technical representative of the Contract Officer in the contract. In order to define and measure quality, the Project Officer has developed a statement of work (SOW) that will accurately define the minimum acceptable requirements for the service. This is the first step in the procurement process that helps to ensure that services produce results or products of acceptable quality. This QA Project Plan and SOPs also state the required data quality. Adherence to the QAPjP and SOPs will be determined through data quality assessments and audits. Other responsibilities of the Project Officer include:

- Assisting in the development of the SOW and QAPjP.
- Reviewing technical and financial progress reports.
- Providing technical direction and act as a technical liaison to GLNPO.
- Monitoring use of government property.
- Certifying vouchers.

The Project Officer will be the first line of contact on technical as well as QA Issues. The Project Officer will be responsible to work with the Contractor and GLNPO staff to ensure that the data collection operation and their resultant data meet the needs of GLNPO.



**Figure 2.1 Lines of communication for data collection activities for the LMMB.**

### 2.2.3 Contractor (EnviroScience) Project Manager

The Contractor Project Manager is the Contractors representative on the Contract. This person is responsible for the contractor staffs adherence to the terms and conditions of the contract which include the SOW, SOPs and the QAPjP. The Project Manager will be made aware of all administrative, technical and QA issues through the Contractor Survey Supervisor or the EPA Project Officer. However, the Project Manager may delegate certain individuals to be technical and QA representatives.

#### 2.2.4 GLNPO QA Manager

The GLNPO QA Manager (QAM) is the delegated manager of the GLNPO QA Program. The main responsibilities of the QAM is QA oversight, ensuring that all personnel understand their QA/QC



responsibilities. The QAM provides technical support and reviews and approves QA products. Responsibilities include:

- Reviewing all acquisition packages (contracts, grants, cooperative agreements, inter-agency agreements) to determine the necessary QA requirements.

- Assisting staff in developing QA documentation and in providing answers to technical questions.

- Ensuring that all environmental data collection activities are covered by appropriate QA planning documentation (e.g., DQOs and QAPjP).

- Ensuring that routinely used sampling and analytical laboratory methods are covered by Standard Operating Procedures (SOPs).

- Ensuring that audits/reviews are accomplished to assure adherence to approved QA plans and to identify deficiencies in QA/QC systems.

- Ensuring that adequate follow-through actions are implemented in response to audit/review findings.

- Tracking the QA/QC status of all programs.

- Assisting in solving QA-related problems at the lowest possible organizational level.

The GLNPO QAM works with the Project Officer and the GLNPO Technical Staff to develop adequate SOPs and the QAPjP.

#### **2.2.5 GLNPO Survey Supervisor**

All the field data collection activities for the LMMB Survey occur onboard the R/V Guardian. The ship runs 24 hours on two 12 hour shifts. Because of the cost to operate the ship and its remote location, technical issues may arise that need immediate attention. The GLNPO Survey supervisor is the technical and QA lead during the survey. This persons responsibilities include:

- Ensuring the adherence of ship requirements (safety etc.), SOPs and the QAPjP by all crew members (EPA and Contractors).

- Modifying technical or QA requirements in an emergency.

- Informing the Contractor Survey Supervisor, Project Officer and QA Manager of any technical or QA modifications.

- Ensuring the performance and/or participating in technical system audits.

During the survey, various EPA staff may serve in this role. Each Survey Supervisor will be responsible for identifying his/her replacement to the Contract Survey Supervisor prior to replacement.

**2.2.6 Contract Survey Supervisor**

This person is the lead for all contractors on the R/V Guardian. This person's responsibilities include:

- Ensuring adherence to all shipboard rules, the contract SOW, SOPs, and QA criteria.
- Informing the GLNPO Survey Supervisor of any technical or QA issues.
- Documenting any technical or QA issues.
- Performing internal technical systems audits.
- Informing contract staff of any technical or QA changes.

**2.2.7 GLNPO Technical Staff**

A number of technical specialists from EPA will also be onboard the R/V Guardian. These persons will be designated as biology and chemistry supervisors for each shift. They are responsible for various parameters listed in Table 1-1. These individuals have developed the SOPs for the data collection activity and will be assisting in the data collection activities. At times these individuals may also be the GLNPO Survey Supervisor. They will be responsible for:

- Assisting in the field data collection activity.
- Informing the GLNPO Survey Supervisor on parameter issues or needed modifications.
- Performing technical system audits.

**2.2.8 Contractor Chief Biologist, Chief Chemist**

These individuals are responsible for ensuring that the activities associated with their titles are performed according to the SOW, SOPs, and QA protocol. Other responsibilities include:

- Assisting in the field data collection activity.
- Informing the GLNPO Survey Supervisor on parameter issues or needed modifications.
- Performing internal technical system audits with the Contract Survey Supervisor.
- Informing their technical staffs of changes in protocol.
- Informing the Contract Survey Supervisor of any technical or QA issues.

### **3.0 QA OBJECTIVES**

This section describes the LMMB SURVEYS QA program which is designed to allow both control and assessment of measurement uncertainty during sampling, preparation/staging, and analyses phases of the survey.

#### **3.1 Data Quality Objectives**

In many instances, data are collected in order to make environmentally sound decisions. Data quality objectives (DQOs) are the full set of performance constraints needed to design a project, including a specification of the level of uncertainty that a decision maker (data user) is willing to accept in the answers to the questions of the study. This is data that, when evaluated, provides the decision maker with enough certainty that he/she is willing to risk making an ~~inappropriate~~ decision. Therefore, the data quality attributes that are associated with data are necessary for any educated ecological management decision.

Uncertainty can be illustrated as follows

$$S_o^2 = S_p^2 + S_m^2 \quad (\text{equation 1})$$

Where:

- o= Overall Uncertainty
- p= Total Population Uncertainty (spatial and temporal)
- m= Measurement Uncertainty (data collection)

The estimate of the overall uncertainty is the DQO and must be defined by the data users. Confidence in estimates of population uncertainty can be controlled through the use of statistical sampling design techniques. The goal of QAPjP is to control measurement uncertainty to an acceptable level through the use of various quality control and evaluation techniques.

#### **3.2 LMMB Survey DQO**

While it is difficult to state the DQO for the LMMB Surveys in statistical terms, the objective of the conventional section of the survey is sampling of the sites chosen for the survey to provide nutrient and biological data to support the eutrophication model component of the Mass Balance Model. The stations for the survey were chosen to provide data for the model to accomplish several purposes: 1) sampling of sufficient offshore and nearshore locations to provide spatial concentration information sufficient for model calibration - within our budget this meant approximately 40 stations, 2) sampling of cross-lake transects, and 3) sampling at 10, 40, and 80 meter depths in delineated biological sampling areas.

As mentioned in the section above. The DQO is the overall uncertainty that the user is willing to accept in the result derived from the data while being able to make an informed decision. This means that both population and measurement uncertainties are understood. This QAPjP will focus on controlling and assessing the measurement uncertainties.

##### **3.2.1 Uncertainty Estimates**

Estimates of both the population and measurement uncertainties of the various measurement

parameters will be needed in order to determine the confidence one has in the final data values. The manner in which these estimates are derived must be statistically valid.

Equation 1 will be used in the evaluation of uncertainty. At present, it is not known what proportion of the uncertainty for the critical pollutants will be attributed to population or measurement. Taylor (1987) suggests that a measured value can be considered error-less for most uses if the uncertainty in that value is one-third or less the permissible tolerance for its use. Since variance is commonly used to express uncertainty, the equation becomes:

$$\text{For: } \underset{\text{(DQO)}}{S_o^2} = \underset{\text{(MQO)}}{S_p^2} + S_m^2 \text{ (equation 1)}$$

$$\text{Taylor: } 10 = 3^2 + 1^2 \quad \text{(equation 2)}$$

$$\text{Or: } 10 = 9 + 1 \quad \text{(equation 3)}$$

Therefore, measurement uncertainty can be assumed to be insignificant if its uncertainty estimate is 1/10 the overall uncertainty. The LMMB SURVEYS can use this equation to determine whether measurement uncertainty needs to be controlled. This process is useful in determining where emphasis should be placed on reducing uncertainties. For example, if the measurement uncertainty is within 1/10 the overall, the data would suggest that management focus on reducing population uncertainty, since little benefit would be derived at reducing measurement uncertainty. The equation serves to identify where to focus QA resources. It should be noticed that the terms data quality objective (DQO) and measurement quality objective (MQO) have been added to equation 1. This serves to distinguish the fact that an MQO is not a DQO and that this QAPjP serves to control the measurement uncertainty by establishing MQOs as defined in section 3.5.

Measurement uncertainty can be further divided to the following components:

$$\underset{\text{(MQO)}}{S_m^2} = \underset{\text{(MQO)}}{S_f^2} + \underset{\text{(MQO)}}{S_{ps}^2} + \underset{\text{(MQO)}}{S_l^2} \text{ (equation 4)}$$

Where:

f = Field

ps= Preparation/Staging

l = Laboratory

Additionally, any one of these components also can be broken into subcomponents for which MQOs can also be developed. For example, laboratory uncertainty can be separated into within run, between run, and among laboratory uncertainties. The level to which uncertainty estimates are separated is initially dependent on whether the overall measurement uncertainty is too great. If so, other estimates are needed to determine where the largest percentage of uncertainty is occurring and how best to reduce this uncertainty.

### 3.3 QA Design

Figure 3.1 is the LMMB SURVEYS design to control and assess data uncertainty for the nutrient category parameters. The first two priorities in developing a QA design are:

- 1) Development of real-time assessment and control.
- 2) Design for an estimate of overall measurement uncertainty.

In order to accomplish the first priority, data must be available for assessment in enough time to make corrections to the data collection system. Often, it is difficult to control field sampling errors in real-time due to the time required to accumulate enough data to make statements of field sampling uncertainty. However, since the WQS is a long term program, information can be gathered prior to next years implementation to reduce uncertainty in future data collection efforts. Another way of developing some real-time control is developing a QA design that verifies data quality in sets or batches that when aggregated will achieve the measurement quality objectives.

The second priority is important for the assessment of the significance of measurement uncertainty to overall uncertainty, as discussed in section 3.3. A QA design must be developed that will allow for an assessment of overall measurement uncertainty. To often more costs than necessary are incurred with assessments of laboratory activities when they are not required. This is not to say that the QA design should only focus on estimates of overall uncertainty; it does say that estimates of this uncertainty are necessary and the design should accommodate this. For the nutrient category parameters, the LMMB SURVEYS incorporates the concept of batch sample analysis, where samples collected in the field are combined into groups called batches. Within these batches, a series of different types of measurement quality samples are included which are used to evaluate and possibly control various types of measurement uncertainty. Figure 3.1 serves to illustrate the use of this design for the nutrient category parameters. This design allows for the verification of a batch of data as well as creates a data set that will allow assessment of the various components (field, preparation and laboratory), and attributes (system detection, precision, etc), as well as the achievement of program DQOs. Figure 3.1 segregates the measurement quality samples into either quality evaluation (QE) or quality control (QC) samples. QE samples are those samples which are known to the GLNPO technical staff but are either blind or double blind to the sampling crews, the preparation laboratory, or the analytical laboratory. A blind sample has a concentration range that is unknown to the analyst, whereas a double blind sample cannot be distinguished from a routine sample and has a concentration range that is unknown (Taylor, 1987). These samples provide an independent check on the QC process and can be used to evaluate whether the MQOs have been met for any given batch, or for all batches. In contrast, QC samples are known to the laboratory staff and can be used by the analysts to identify and control analytical measurement uncertainty. The following section provides information on these objectives.

### **3.4 Measurement Quality Objectives**

Measurement quality objectives are designed to control various phases of the measurement process and to ensure that total measurement uncertainty is within ranges prescribed by the DQOs. The MQOs can be defined in terms of precision, accuracy, completeness, detectability, representativeness, and comparability. The first four can be defined in a quantitative terms, as illustrated in Tables 3-1 - 3-3, while the latter two are qualitative. Descriptions of the terms, and the types of samples that will be used for assessment criteria are explained below. The types of samples identified here are from a larger list of QE/QC samples which are defined in Appendix G of the GLNPO Quality Management Plan. The codes will be used when identifying these samples in the LMMB SURVEYS data base.

**Precision** - A measure of mutual agreement among multiple measurements of the same property, usually under prescribed similar conditions. Precision will be evaluated through auditing of data collection activities to determine whether activities are performed in a consistent manner, and by established protocol. The following types of samples will be used to determine precision at various measurement phases:

Field Duplicates (FD1, FD2 etc.) - two or more environmental samples taken at the same time (in the case of two sample collection devices) or sequentially (one sampling device) and in the same place under identical circumstances. Each sample is treated identically throughout field and laboratory analytical procedures; and each is carried through the entire laboratory analytical method as applied to all other samples analyzed with the same method. These samples can be used to assess overall data

collection precision. However, these samples contain a component of population variability.

Field Split Samples (FS1, FS2, etc.) - two or more samples that are split from an original sample. The sample is thoroughly homogenized before splitting. Each sample is treated identically throughout preparation and laboratory analytical procedures; and each is carried through the entire laboratory analytical method as applied to all other samples analyzed with the same method. These samples can be used to assess overall data collection precision. Although this sample theoretically does not contain population uncertainty, it also does not contain the full component of measurement uncertainty since each sample was not processed through the full data collection system.

Laboratory Split Sample (LS1, LS2, etc.) - The same definition of Field Split Samples with the exception of occurrence in the laboratory. These samples can be used to assess laboratory within batch precision.

Laboratory Reference Sample (LR1, LR2, etc.) An aliquot of a sample (submitted by the requestor) having a certified value. These samples are usually obtained from a vendor (NIST etc.) or a cooperator (NWR1, EMSL-CIN). The concentration measured by the same analytical procedure used for other samples is the "found" value. Since these are paired samples, they can be used to assess within batch and between batch precision. The sample can also be used to assess accuracy.

Laboratory Performance Check Solution (LPC)- A solution of method analyte(s), surrogate(s) and/or internal standard(s) used to evaluate the performance of an instrument with respect to a defined set of criteria. Two pairs of samples at a high and low concentration will be inserted into the batch. They can be used to assess within batch and between batch precision. The samples can also be used to assess accuracy.

**Accuracy** - The degree of agreement between a measurement (or an average of measurements of the same thing), and the amount actually present. The following types of samples will be collected to determine accuracy at various measurement phases:

Field Blank (FRB) - An aliquot of reagent water or equivalent neutral reference material treated as an environmental standard sample in all aspects in the laboratory including addition of reagents, internal standards, surrogates, glassware, apparatus, equipment, solvents, and analyses. The FRB is used to identify any system contamination.

Laboratory Calibration Blank (LCB) - An aliquot of reagent water, possibly adjusted in pH, but without addition of other reagents. Will be used to identify laboratory process contamination.

Laboratory (reagent) Blank (LRB) - An aliquot of reagent water or equivalent neutral reference material treated as an environmental standard sample in all aspects in the laboratory including addition of reagents, internal standards, surrogates, glassware, apparatus, equipment, solvents, and analyses. Will be used to identify laboratory process contamination.

Field Reference Samples (FR1, FR2 etc) - The same definition of Laboratory Reference Samples with the exception of occurrence in the field. Can be used to identify system contamination.

Laboratory Performance Check Solution (LPC)- A solution of method analyte(s), surrogate(s) and/or internal standard(s) used to evaluate the performance of an instrument with respect to a defined set of criteria.

Laboratory Reference Solution (LRM) -An aliquot of a sample (submitted by the requestor) having a certified value. These samples are usually obtained from the NBS, EMSL, etc. The concentration measured by the same analytical; procedure used for other samples is the "found" value.

**Completeness** - For this QAPP completeness is the measure of the number of valid samples obtained compared to the amount that is needed to meet the DQOs. The LMMB SURVEYS completeness goal is 95%.

**Representativeness** - Expresses the degree to which data accurately and precisely represent characteristics of a population, parameter variations at a sampling point, a process condition, or an environmental condition. Representativeness with respect to the present study is a measure of the parameter variation at a sampling point and is evaluated by collecting random duplicate samples.

**Detectability** - The determination of the low-range critical value of a characteristic that a method-specific procedure can reliably discern. Three types of detection limits are important to address in the LMMB SURVEYS; the system detection limit (SDL), the method detection limit (MDL), and the instrument detection limit (IDL). The following types of samples will be collected to determine these types of detection limits

Field Blank (FRB) - See definition above. Pooled FRB data can be used to develop a system detection limit (SDL), which is calculated as three times the standard deviation of the FRB sample.

Laboratory Calibration Blank (LCB) - See definition above. Will be used to identify and control laboratory process contamination. LCBs can be pooled and used, if necessary, for background correction.

Laboratory (reagent) Blank (LRB) - See definition above. Will be used to identify and control laboratory process contamination and may be used to determine an on-going MDL.

Laboratory Control Solution (LCM) - An aliquot of reagent water or equivalent neutral reference material to which a known quantity(s) of method analytes(s) was added in the laboratory. The LCM is treated as an environmental sample in all aspects in the laboratory including addition of all reagents internal standards, surrogates, glassware, equipment, solvents, and analyses. This sample is used to determine the method detection limit as defined in 40 CFR Appendix B Part 136. This sample is not run with every batch.

Instrument Detection Limit Solution (IDL) - A calibration solution where data is used to calculate the instrument detection limits only.

**Comparability** - Express the confidence with which one data set can be compared to another. The comparability of one years data with another is maintained by adherence to standard operating procedures. When a procedure or an instrument is changed, a comparison is made to verify that the data is identical or more precise or accurate.

**Table 3-1 Measurement Quality Objectives for LMMB SURVEYS Nutrient Category**

Parameter	Sample Type	Frequency	Acceptance Criteria
Total Kjeldahl N Precision	FD1	1/bat	$\bar{A} < 0.15$ if mean $< 0.37$ or RPD $< 40$ if mean $> 0.37$
	FS1	ch	$\bar{A} < 0.10$ if mean $< 0.33$ or RPD $< 30$ if mean $> 0.33$
	LS1	1/bat	$\bar{A} < 0.05$ if mean $< 0.25$ or RPD $< 20$ if mean $> 0.25$
	LR1/2	ch	$\bar{A} < 0.05$ if mean $< 0.25$ or RPD $< 20$ if mean $> 0.25$
Accuracy	LPC	1/bat	$\bar{A} < 0.05$ if mean $< 0.25$ or RPD $< 20$ if mean $> 0.25$
	Pairs	ch	Mean within accuracy windows
	IPC	1	Mean within accuracy windows

Completeness Detectability	Pairs LR1/2 FR1 Routine samples LRB LCB FRB	pair/batch 2 pairs/batch 2 pairs/batch 1 pair/batch 1/bat ch  1/bat ch 1/bat ch 1/bat ch	Value within accuracy windows 95 % > ___ AND < RMDL > ___ AND < RMDL > ___ AND < 2*RMDL
Nitrate + Nitrite N Precision   Accuracy  Completeness Detectability	FD1 FS1 LS1 LR1/2 LPC Pairs LPC Pairs LR1/2 FR1 Routine samples LRB LCB FRB	1/bat ch 1/bat ch 1/bat ch 1 pair/batch 2 pairs/batch 2 pairs/batch 1 pair/batch 1/bat ch  1/bat ch 1/bat ch 1/bat ch	$\bar{A} < 0.15$ if mean < 0.37 or RPD < 40 if mean > 0.37 $\bar{A} < 0.10$ if mean < 0.33 or RPD < 30 if mean > 0.33 $\bar{A} < 0.03$ if mean < 0.15 or RPD < 20 if mean > 0.15 $\bar{A} < 0.03$ if mean < 0.15 or RPD < 20 if mean > 0.15 $\bar{A} < 0.03$ if mean < 0.15 or RPD < 20 if mean > 0.15 Mean within accuracy windows Mean within accuracy windows Value within accuracy windows 95 % > ___ AND < RMDL > ___ AND < RMDL > ___ AND < 2*RMDL
Total P Precision   Accuracy  Completeness Detectability	FD1 FS1 LS1 LR1/2 LPC Pairs LPC Pairs LR1/2 FR1 Routine samples LRB LCB FRB	1/bat ch 1/bat ch 1/bat ch 1 pair/batch 2 pairs/batch 2 pairs/batch 1 pair/batch 1/bat ch  1/bat ch 1/bat ch 1/bat ch	$\bar{A} < 0.010$ if mean < 0.04 or RPD < 25 if mean > 0.04 $\bar{A} < 0.005$ if mean < 0.03 or RPD < 15 if mean > 0.03 $\bar{A} < 0.002$ if mean < 0.02 or RPD < 10 if mean > 0.02 $\bar{A} < 0.002$ if mean < 0.02 or RPD < 10 if mean > 0.02 $\bar{A} < 0.002$ if mean < 0.02 or RPD < 10 if mean > 0.02 Mean within accuracy windows Mean within accuracy windows Value within accuracy windows 95 % > ___ AND < RMDL > ___ AND < RMDL > ___ AND < 2*RMDL
Total Dissolved P			



Precision	FD1	1/bat	$\bar{A} < 0.010$ if mean $< 0.04$ or RPD $< 25$ if mean $> 0.04$
	FS1	ch	$\bar{A} < 0.005$ if mean $< 0.03$ or RPD $< 15$ if mean $> 0.03$
	LS1	1/bat	$\bar{A} < 0.002$ if mean $< 0.02$ or RPD $< 10$ if mean $> 0.02$
	LR1/2	ch	$\bar{A} < 0.002$ if mean $< 0.02$ or RPD $< 10$ if mean $> 0.02$
	LPC	1/bat	$\bar{A} < 0.002$ if mean $< 0.02$ or RPD $< 10$ if mean $> 0.02$
Accuracy	Pairs	ch	Mean within accuracy windows
	LPC	1	Mean within accuracy windows
	Pairs	pair/batch	Value within accuracy windows
Completeness	LR1/2	2	95 %
Detectability	FR1	pairs/batch	$> \text{___ AND } < \text{RMDL}$
	Routine	2	$> \text{___ AND } < \text{RMDL}$
	samples	pairs/batch	$> \text{___ AND } < 2*\text{RMDL}$
	LRB	1	
	LCB	pair/batch	
	FRB	1/bat	
		ch	
		1/bat	
		ch	
		1/bat	
		ch	
		1/bat	

Table 3-1. (Continued)

Parameter	Sample Type	Frequency	Acceptance Criteria
Chloride			
Precision	FD1	1/bat	$\bar{A} < 0.6$ if mean $< 3.0$ or RPD $< 20$ if mean $> 3.0$
	FS1	ch	$\bar{A} < 0.4$ if mean $< 2.7$ or RPD $< 15$ if mean $> 2.7$
	LS1	1/bat	$\bar{A} < 0.2$ if mean $< 2.0$ or RPD $< 10$ if mean $> 2.0$
	LR1/2	ch	$\bar{A} < 0.2$ if mean $< 2.0$ or RPD $< 10$ if mean $> 2.0$
	LPC	1/bat	$\bar{A} < 0.2$ if mean $< 2.0$ or RPD $< 10$ if mean $> 2.0$
Accuracy	Pairs	ch	Mean within accuracy windows
	LPC	1	Mean within accuracy windows
	Pairs	pair/batch	Value within accuracy windows
Completeness	LR1/2	2	95 %
Detectability	FR1	pairs/batch	$> \text{___ AND } < \text{RMDL}$
	Routine	2	$> \text{___ AND } < \text{RMDL}$
	samples	pairs/batch	$> \text{___ AND } < 2*\text{RMDL}$
	LRB	1	
	LCB	pair/batch	
	FRB	1/bat	
		ch	
		1/bat	
		ch	
		1/bat	
		ch	
		1/bat	
		ch	
Total Suspended Solids			
Precision	FD1	1/bat	$\bar{A} < 0.90$ if mean $< 3.0$ or RPD $< 30$ if mean $> 3.0$
	FS1	ch	$\bar{A} < 0.75$ if mean $< 3.8$ or RPD $< 20$ if mean $> 3.8$
	LS1	1/bat	$\bar{A} < 0.54$ if mean $< 3.6$ or RPD $< 15$ if mean $> 3.6$
	LR1/2	ch	$\bar{A} < 0.54$ if mean $< 3.6$ or RPD $< 15$ if mean $> 3.6$
	LPC	1/bat	$\bar{A} < 0.54$ if mean $< 3.6$ or RPD $< 15$ if mean $> 3.6$
Accuracy	Pairs	ch	Mean within accuracy windows
	LPC	1	Mean within accuracy windows
	Pairs	pair/batch	Value within accuracy windows
Completeness	LR1/2	2	95 %
Detectability	FR1	pairs/batch	$> \text{___ AND } < \text{RMDL}$

		Routine samples	2 pairs/batch	> ____ AND < RMDL > ____ AND < 2*RMDL
		LRB LCB FRB	1 pair/batch 1/bat ch  1/bat ch 1/bat ch 1/bat ch	
Reactive Si Precision		FD1 FS1 LS1 LR1/2 LPC	1/bat ch 1/bat ch 1/bat	$\bar{A} < 0.035$ if mean < 0.12 or RPD < 30 if mean > 0.12 $\bar{A} < 0.025$ if mean < 0.12 or RPD < 20 if mean > 0.12 $\bar{A} < 0.015$ if mean < 0.1 or RPD < 15 if mean > 0.1 $\bar{A} < 0.015$ if mean < 0.1 or RPD < 15 if mean > 0.1 $\bar{A} < 0.015$ if mean < 0.1 or RPD < 15 if mean > 0.1
Accuracy	Pairs	LPC	1 pair/batch	Mean within accuracy windows Mean within accuracy windows Value within accuracy windows
Completeness Detectability	Pairs	LR1/2 FR1 Routine samples	2 pairs/batch 2 pairs/batch 1 pair/batch 1/bat ch  1/bat ch 1/bat ch 1/bat ch	95 % > ____ AND < RMDL > ____ AND < RMDL > ____ AND < 2*RMDL

**Table 3-2. Measurement Quality Objectives for LMMB SURVEYS Physical Category**

Parameter	Sample Type	Frequency	Acceptance Criteria
Temperature Air Precision Accuracy Completeness  Water Precision Accuracy Completeness			
Wind Speed Precision Accuracy Completeness			
Wind Direction Precision Accuracy Completeness			
Water Clarity Precision Accuracy Completeness			
Wave Height Precision Accuracy Completeness			
Optical Transmittance Precision Accuracy Completeness			
Turbidity Precision Accuracy Completeness			
Specific Conductance Precision Accuracy Completeness			
pH Precision Accuracy Completeness			

**Table 3-3. Measurement Quality Objectives for LMMB SURVEYS Biological Category**

Parameter	Sample Type	Frequency	Acceptance Criteria
Dissolved Oxygen Precision Accuracy Completeness			
Phytoplankton Precision Accuracy Completeness			
Zooplankton Precision Accuracy Completeness			
Aerobic Heterotrophs Precision Accuracy Completeness			
Chlorophyll "a" Precision Accuracy Completeness			

**Figure 4.1 Minimum QE/QC requirements for Each Batch of LMMB SURVEYS Samples (maximum batch size = 40 including QE/QC)**

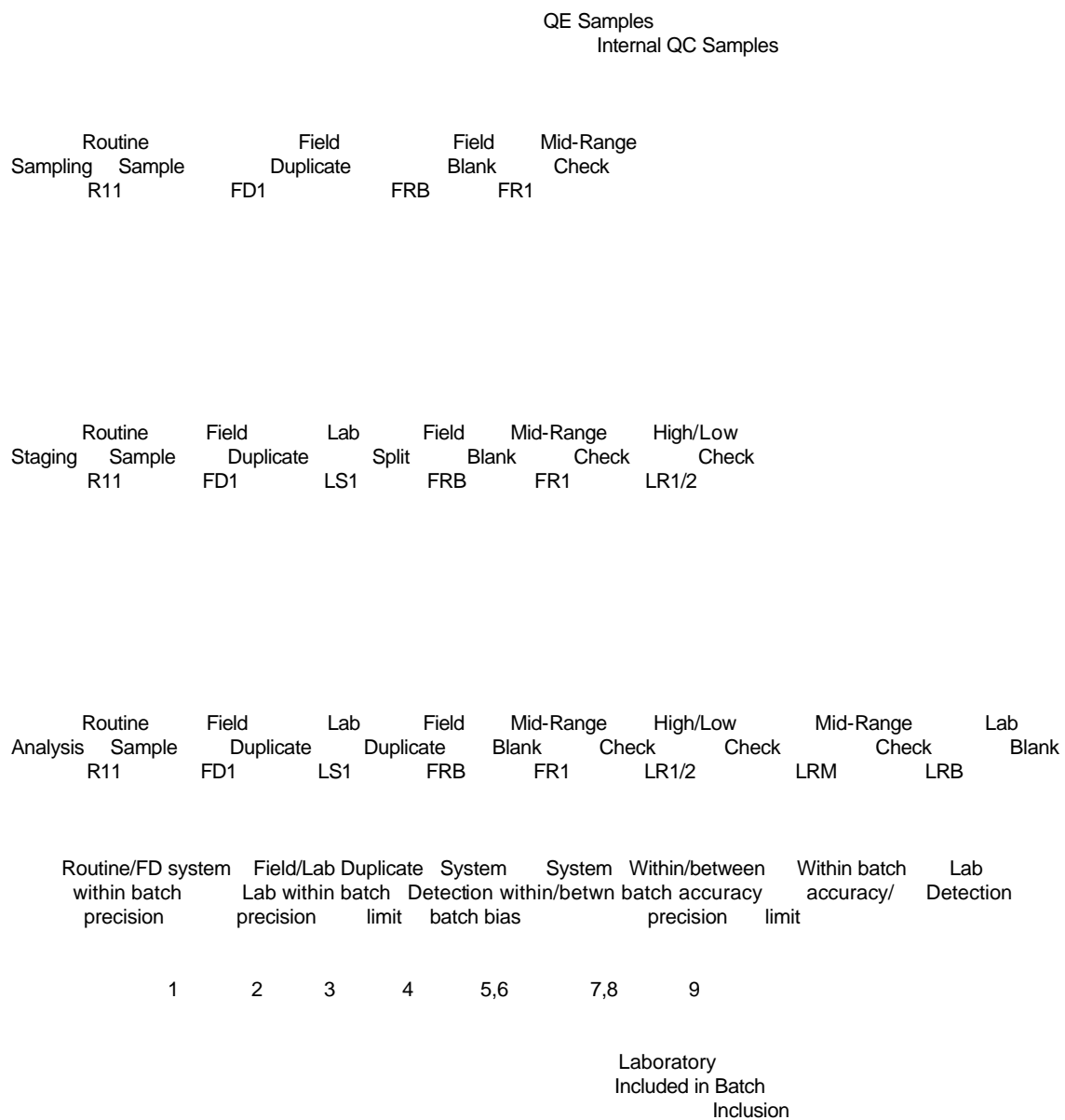


Table 3-1. QA OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY, COMPLETENESS, REPRESENTATIVENESS AND COMPARABILITY

PARAMETER	PRECISION GOAL		COMPLETENESS GOAL	
	From Duplicate Analysis		GOAL	
	$ x_1 - x_2 $ or 8% whichever is larger	diff	ACCURACY GOAL	GOAL
Air Temperature	0.5°C	0.5°C	100%	
Wind Speed	1 nautical mph	(1 nautical mph + 20%) times measured value	100%	
Wind Direction	10°	10°	100%	
Secchi Depth	.5 m	(.2 m + 20% times measured value)	100%	
Wave Height	.5 m	(.3 m + 30% times measured value)	100%	
Water Temperature	.1°C	0.5°C	100%	
Optical Transmittance		5%	95%	
Turbidity	0.12	.18   (0.1 + 10% times measured value)	95%	
Specific Conductance	.5uS	.5uS   (control std.) x 3s	95%	
pH	.2SU	.6SU   (control std.) x 3s	95%	
Total Alkalinity	.6mg/L	0.8mg/L   (control std.) x 3s	95%	
Total Ammonia Nitrogen	.5ppb	0.5ppb   (control std.) x 3s	95%	
Total Kjeldahl Nitrogen	20ppb	22ppb   (control std.) x 3s	95%	
Dissolved Nitrate & Nitrite	3ppb	3ppb   (control std.) x 3s	95%	
Total Phosphorus	.6ppb	1ppb   (control std.) x 3s	95%	
Dissolved Orthophosphate	.6ppb	1ppb   (control std.) x 3s	95%	
Total Chloride	.2ppm	0.5ppm   (control std.) x 3s	95%	
Total Sulfate	.3ppm	0.5ppm   (control std.) x 3s	95%	
Total Dissolved Phosphorus	.6ppb	1.0ppb   (control std.) x 3s	95%	
Dissolved Reactive Silica	5ppb	8ppb   (control std.) x 3s	95%	
Particulate Organic Carbon	< ( + 2s)	(control std.) x 3s	95%	
Dissolved Organic Carbon	not established	not established	95%	
Na		x 2s	95%	
K		x 2s	95%	
Ca		x 2s	95%	
Mg		x 2s	95%	
Dissolved Oxygen	.2 ppm	0.6ppm   0.5 mg/L or times measured value	10%   95%	
Phytoplankton	see method varies with algae type	NA	95%	
Zooplankton	not established	NA	95%	

Aerobic Heterotrophs	not established	NA		95%
Chlorophyll "a"	RPD < 7%	10% or .3 ug/L		95%
	whichever is greater			

NA = Not Applicable

RPD = Relative Percent Difference

= difference between duplicates (lab splits) =  $\frac{\sum_{i=1}^m |x_i - \bar{x}|}{n}$  where  $x_i$  and  $\bar{x}$  are duplicate samples

= average difference between lab splits

samples

## **4.0 Sampling Procedures**

The following sections will briefly describe some of the aspects of field sampling for the LMMB Surveys. A listing of the sampling equipment and the methods are found in Table 1-2. Detailed methods can be found in WQS Field and Analytical Methods Manual.

### **4.1 Training and Certification**

The survey scientists provided by the Contractor will be trained at the Central Regional Laboratory (CRL). All instrumentation will be assembled and tested at the CRL before it is sent to the R/V Lake Guardian for each survey. Testing will consist of checking all control standards on the assembled systems to (1) verify proper concentration, and (2) demonstrate that all analytical systems to be used on the RV Lake Guardian are capable of running within the limits required using the current standards.

After the equipment is installed on the R/V Lake Guardian, the Contractor's QC Coordinator will accompany the Contractor's survey staff while they test all sampling and analytical equipment prior to beginning the survey. The entire sampling process is implemented. At that time, the QC Coordinator and the GLNPO Survey Supervisor will evaluate the procedures and analytical systems to determine the status of the equipment and personnel readiness.

### **4.2 Sampling Equipment**

#### **4.2.1 Rosette Sampler**

The Rosette sampler is the primary sampling instrument for the collection of all Nutrient Category parameters, phytoplankton, chlorophyll a, phaeophytin a, and dissolved oxygen from the Biological Category, and temperature, total suspended solids, turbidity, specific conductance, and pH from the Physical Category.

A 12-bottle Rosette sampler system (General Oceanics Model 1015-12-8) will be used to collect water samples. A submersible bottle mounting array enables an operator to remotely actuate a sequence of up to 11 water sampling bottles. This system consists of an electronic bathythermograph (EBT-Guideline Model 8705) attached to the twelfth bottle position of the array, an A-frame, 1000 feet of multi-conductor cable, and a 5HP variable speed winch. The EBT measures water depth and temperature, which is graphically displayed onboard the research vessel. The bottles can be sequentially closed remotely from the deck of the vessel while the array is submerged at the various sampling depths. The Rosette will accommodate any of the General Oceanics rigid PVC 1010 Niskin sampling bottles up to the 8 liter size. GLNPO uses the 8 liter bottles.

The Guideline EBT is factory calibrated, so that the only way that erroneous values can be obtained are through improper placement of the suppression, zero, volts/unit controls, or the recorder controls. A variable zero control for the depth (pressure) is necessary to compensate for atmospheric pressure variability. The zero control for temperature should not be manipulated once it is properly set with an ice water bath prior to the cruise (Guideline manual). Temperature will be plotted along the horizontal axis at 50 ft/in. to 500 ft. at which point the scale will be shifted to 125 ft/in. After the samples are collected and the Rosette is brought on board by use of the A-frame, the samples are distributed to the various sample storage bottles while the Niskin bottles remain attached to the Rosette. The sample distribution is described in Figures 4.1 and 4.2.

The depth at which samples will be collected is determined by a pressure transducer on the Rosette sampler. To assure that the controls on the depth measuring equipment are properly set, the bottom sounding will be compared to the Rosette sample reading at each station. The Rosette winch operator obtains a depth sounding from the bridge and writes this on the chart under observations and marks the chart at the appropriate location on the depth axis edge. The Rosette sampler will then be raised. Three minutes will pass to allow the sampler to drift away from the disturbed area before the B-2 (2 meters up from the bottom) sample is taken. The Rosette sampler will be lowered to B-2 and the sample taken.



A duplicate sample will be taken prior to the B-2 sample. Additional time intervals of three minutes are allowed to elapse prior to taking the thermocline sample and the lower epilimnion sample. These intervals provide time for water equilibration within the Niskins.

The knees of the EBT temperature depth trace will be determined by trisecting the angle between the epilimnion and mesolimnion temperature traces (upper knee) and the angle between the mesolimnion and hypolimnion temperature traces (lower knee). The upper knee is the upper 1/3 angle intercept, the lower knee is the lower 1/3 angle intercept. The lower epilimnion sample is one meter above the upper knee. The upper hypolimnion sample is one meter below the lower knee.

#### **4.2.2 X,Y Plotter-Hewlett Packard Model 7046A**

Since the selection for sampling depths is influenced by the temperature-depth profile, the temperature vs. depth graph is recorded by an x,y plotter (HP Model 7046A) as the Rosette is lowered to the bottom. Collection of the samples is done primarily as the Rosette is raised to the surface. Care should be taken to assure that the HP recorder vernier controls (on the range selector switches) are set on the cal position, and that the suppression controls on the Guideline console are set at zero.

### ***4.3 Sequence of Sampling Events***

The following is a brief summary of the sampling events. Some events may be done simultaneously and event order will be subject to conditions.

#### **1. Visual and Physical Station Observations**

Air temperature, wind speed, aesthetics, wind direction, depth, and wave height.

#### **2. Rosette Sampling**

Run EBT down to define the temperature profile and determine the thermocline location during stratified situations

Examine the EBT profile. Select sampling depths according to depth selection.

Trigger sample bottle at correct depths, while verifying the temperature profile

Split Rosette Niskin samples into the required sample bottles/preservatives. (See Figures 4-1 and 4-2 for details)

A composite 20m sample is taken for phytoplankton, chlorophyll a, pheophytin, DOC and POC by compositing Niskin samples at 1, 5, 10 and 20 meters.

#### **3. Zooplankton Sampling**

Conduct the 20 meter and B-2 vertical tows for zooplankton samples, rinse net and pour into 500 ml. polyethylene bottles with 10-15 ml club soda and 5% formalin as preservatives.

#### **4.3.1 Sample Integrity**

Concentration of chemicals in lake water are very dilute. A small amount of sample contamination can have a large effect on the results. Avoiding contamination is, therefore, a major quality control goal. Each Niskin sampling bottle shall be emptied into the sample bottles as soon as possible. All chemistry sample bottles shall be rinsed once with sample before filling. New one gallon polyethylene containers (PEC) will be used to hold the sample for the on board analyses and preparations.

One gallon polyethylene containers filled directly from Niskin sampling bottles are used for total nutrients, pH, specific conductance, alkalinity and turbidity analyses. Samples for analysis of dissolved nutrients are taken from the one-gallon containers and filtered into new 125-ml sample bottles.

Samples for chlorophyll a analysis are collected directly from Niskin sampling bottles into 300-ml brown polyethylene sampling bottles. Water to be used for primary productivity analysis taken directly from Niskin sampling bottles into 960-ml polyethylene bottles. These samples are composited into darkened cubitainers.

To reduce contamination from atmospheric dust, empty bottles will be capped during preparation for sampling. Care should also be taken in the storage of bottles to reduce exposure to "dirty" environmental conditions. During sampling, each bottle is rinsed with sample water, emptied, and filled with sample water. The cap is replaced after addition of the preservative, or immediately on samples that require no preservative. Transfer of the samples from one container to another or manipulations of the sample are avoided as much as possible since each such action can result in contamination.

To reduce contamination and to control the volume of the preservatives, automatic pipettes or dispensers are used to dispense all preservatives. Prevention of inadvertent use of the wrong preservative is accomplished by the use of the same color tag on the sample bottle and preservative dispenser. Dissolved oxygen samples are "set up" immediately. This involves filling the bottle to overflowing, allowing overflowing to continue 5 seconds before adding, in series, the first two reagents, allowing the floc to settle, mixing and allowing floc to settle again. D.O. samples are then completed in the main laboratory.

#### **4.4 Sample Filtration**

A number of samples must be filtered, after sample splitting (Figure 4.1 and 4.2). The following are brief summaries.

##### **4.4.1 Nutrient Sample Filtration**

Dissolved nutrient samples will be prepared by vacuum filtration (< 7 psi) of an aliquot from the PEC for onboard analyses within an hour of sample collection. A 47 mm diameter 0.45 um membrane filter (Sartorius) held in a polycarbonate filter holder (Gelman magnetic) with a polypropylene filter flask prewashed with 100 to 200 ml of demineralized water or sample water will be used. New 125 ml polyethylene sample bottles with linerless closures will be rinsed once with filtered sample prior to filling.

#### **4.5 Sample Collection**

The Physical Category contains parameters in which direct measurement or observation occurs. They will be briefly summarised. The remainder of the Nutrient, Biological and Physical parameters will be further discussed in the Sample Analysis section. A list of parameters analyzed may be found in Table 4-1. Detailed analytical methods are in WQS Field and Analytical Methods Manual.

##### **4.5.1 Air Temperature**

Air temperature will be determined by use of the Maxi-Min. Temperature System RMS-Technology Inc. which will be read to the nearest 0.1°C.

##### **4.5.2 Wind Speed and Direction**

Wind speed and direction readings from a permanently mounted Danforth Marine type Wind Direction and Speed Indicator or a Wind Speed and Wind Direction Meteorological Meter Model F will be taken and recorded while the vessel is stopped to the nearest 1° (to the right of true north). Wind direction is accurate to 10°. The reading of speed will be estimated to the nearest nautical mile per hour and stored as miles per hour.

#### **4.5.3 Water Clarity**

Secchi Disc Depth will be estimated at each station on all cruises by use of a 30 cm, all-white Secchi disc. Secchi disc depths will be recorded to the nearest 0.5 meters.

#### **4.5.4 Wave Height**

Average wave height (valley to crest distance) and wave direction will be estimated at each station by the senior crew member on the bridge. Wave heights will be recorded to the nearest 0.5 ft.

#### **4.5.5 Water Temperature**

EBT temperature will be verified by use of a mercury thermometer readable to 0.1°C (ASTM no. 90C). The thermometer shaft will be immersed in the surface water Niskin bottle or in the 960 ml plastic sample bottle. Readings will be estimated to the nearest 0.1°C. EBT temperature trace data will be used for in situ temperature readings for all sampling depths. The Niskin sampling bottles used on the Rosette may be fitted with Reversing Thermometer Assemblies (one on every other bottle) for use as a check on the EBT temperature probe readout.

#### **4.5.6 Water Temperature and Light Transmission Profiles**

Temperature vertical profiles may be determined from surface to bottom with the Sea Bird CTD.

The turbidity sensor uses a transmissometer technique of light attenuation. The sensor utilizes a constant LED light source and calibrated photosensor separated by a 25 centimeter path length. The attenuation of the light source by the turbid water is measured. The measurement is indicated in terms of percent transmission, or alternatively as an attenuation coefficient.

#### **4.5.7 Aesthetics**

Reports of any unusual visual conditions that exist at any station will be made. Conditions such as floating algae, detritus, dead fish, oil, unusual water color, or other abnormal conditions will be recorded in the field observations.

**Table 4-1 Parameter List Including Sampling Information**

Parameter	STORET	Cruise	Stations	Depth	Sample
<b>Nutrients</b>					
Total Alkalinity	00410	All	All	All	Niskin PEC
Total Kjeldahl N	00625	"	"	"	" - 125 PE(S)
Diss. Nitrate+Nitrate N	00631	"	"	"	" - 125 PE
Total Phosphorus	00665	"	"	"	" or 125 PE
Total Dissolved P	00666	"	"	"	" - 125 PE
Chloride	00940	"	"	"	"
Diss. Reactive Silica	01140	"	"	"	" - 125 PE
<b>Physical</b>					
Aesthetics		All	All	All	Onsite Measure
Temperature					
Air	00020	All	All	—	Shaded from sun
Water	00010	"	"	All	Niskin,EBT,CTD
Wind Speed	00035	"	"	—	Onsite measure
Wind Direction	00040	"	"	—	"
Water Clarity	00078	"	"	—	"
Wave Height	70222	"	"	—	"
Wave Direction		"	"	—	"
Optical Transmittance	00074	"	"	Continuous	CTD
Turbidity	00076	"	"	All	Niskin PEC
Dissolved Oxygen	00300	"	"	"	"
Specific Conductance	00095	"	"	"	"
pH	00040	"	"	"	"
<b>Biological</b>					
Phytoplankton		All	All	Integrated	Niskin-960PE(L)
Zooplankton		"	"	"	#6net-500PE(C)
Chlorophyll <b>a</b>	32209	"	"	"	Niskin-PEC
Phaeophytin <b>a</b>	32213	"	"	"	"
Primary Prod. Parameters		"	Selected	Selected	Niskin - PEC

EBT - Electronic Bathythermograph

CTD - Conductivity-Temperature-Depth (Sea Bird)

PEC - Polyethylene Cubitainer, 4 liter

PE - Polyethylene, preceding number indicates volume in milliliters

(S) - 1ml/l concentrated sulfuric acid added as preservative

(N) - 5ml/l concentrated nitric acid added as preservative

(L) - 8-10 ml/l Acid Lugols preservative

(C) - Club soda, 5% formalin

## 4.6 Holding Times

Maximum holding times, preservation or storage methods, and ship board operational storage methods and holding times are displayed in Table 4-2.

**Table 4-2 Sample Preservation and Holding Times**

Parameter	Max. Holding time Unpreserved	Preservation/Storage Method	Max. Holding Time Preserved	Operational Storage Method and Holding Time Limits
Turbidity	unstable	Refrigerate 4 °C	48 Hr (1)	2 hr.
Dissolved Oxygen	perform ASAP	None	8 hr. (1)	1st 2 reagents immediately Add Acid within 8 hr. Titrate within 30 min. of acid addition
Specific Conductance		Refrigerate 4 °C	28 days (1)	2 hr.
pH		None	2 hr. (1)	2 hr.
Alkalinity		Refrigerate 4 °C	14 days (1)	2 hr.
TKN		1 ml H <sub>2</sub> SO <sub>4</sub> /L	28 days (1) 90 days (2)	At CRL < 90 days
NO <sub>3</sub> - NO <sub>2</sub> & TDP	24 hr	1 ml H <sub>2</sub> SO <sub>4</sub> /L in filtered sample (Orange label)	28 days (1) 90 days (2)	48 hr. (4 C) at CRL < 90 days
Total Phosphorus	24 hr.	1 ml H <sub>2</sub> SO <sub>4</sub> /L in unfiltered sample (Yellow label)	28 days (1) 90 days (2)	At CRL < 90 days
Chloride	indefinite	None	28 days (1)	indefinite
SiO <sub>2</sub>	indefinite	None	28 Days (1)	48 hr. (4 C)
Particulate Organic C			not established	At CRL not established
Dissolved Organic C	48 hr.	1 ml H <sub>2</sub> SO <sub>4</sub> /L	28 days (1) 90 days (2)	48 hr.
Sample Filtration	ASAP	None		1 hr.

(1) EPA CFR, Part 136 Holding Time.

(2) Recommendation of EPA CRL. Although there are no data to indicate the this type of sample is unstable, a 90-day holding time is recommended.

## 5.0 SAMPLE CUSTODY

Strict chain-of-custody procedures do not apply for LMMB SURVEY samples. None of the lake data is intended to be used for litigation. However, sample custody procedures are also used to ensure the integrity of sample and therefore the process must be documented.

Prior to each survey, numbered sample bottle labels will be printed by computer. The sample bottle label will contain the following information:

CRL sample number (see below)  
 Lake  
 Station number  
 Survey date  
 Preservation used  
 Parameter to be measured  
 QC sample depth

CRL sample numbers are of the following format:

Year	- <u>G</u> -	-	Series	-	-
	Sample Device	Lake		Sample Type	Sample Number

Valid codes follow:

<i>Year</i>	<i>Sample Device</i>	<i>Lake</i>	<i>Series</i>	<i>Sample Type</i>	<i>Sample</i>
	<i>Number</i>				
93	G-Grab	A- Michigan	???	S- Primary	00-12
94		B- Huron			I- Integrated
		C- Erie		D- Duplicate	
		D- Connecting Channels		R- Field Blank	
		E- Ontario		C- Dup. Analysis	
				X- Spike	
					B- Lab. Blank

Labels will be color coded to indicate the preservation used, and to identify filtered samples i.e., yellow for sulfuric acid (total nutrient), orange for sulfuric acid (total dissolved nutrients), green for nitric acid (metals), and white for unpreserved.

Prior to arrival at a sampling station, those station labels will be segregated and applied to the sampling bottles. When sample bottling and preservation are completed, a record of the numbers on the labels used will be made on analysis request sheets. The analysis request sheet will be used to track samples through the processing and analysis stages.

All on-board results will be recorded in data files on floppy diskettes on the on-board Intel computer. Back-up diskettes will be updated at the end of each shift. Master sheets will also be available for data recording as needed (samples attached) (Figures 5-1A to 5-1C). Physical parameters will be recorded on similar sheets (sample attached) (Figure 5-2). Results generated at the CRL will be reported on CRL data forms.

## 6.0 Calibration Procedures and Frequency

Calibration methods for each parameter are provided in the Field and Analytical Methods Manual. Table 6-1 provides a brief summary.

**Table 6-1. Calibration Procedures and Frequency**

INSTRUMENT	REFERENCE OF CALIBRATION PROCEDURE	CALIBRATION STANDARD	FREQUENCY
EBT Guildline Model 8705	Factory Calibrated	Factory Calibrated	2 Years
Maxi-Min Temp. System, RMS Technology, Inc	"	"	"
Danforth Marine Indicator - Wind Speed and Direction, Meteorological Meter Model F	"	"	"
Secchi Disk			
Turner Turbidimeter	None Required	"	"
YSI Model 35 Conductivity Bridge	Instrument Manual	Formazin	Daily
Jenco 6071 pH Meter	Instrument Manual	Shunts	—
Cole Parmer 5997 pH Meter	Instrument Manual	Buffers pH 7 and pH 10	Daily
Lachat - NH <sub>3</sub>	Instrument Manual	Buffers pH 4 and pH 7	Daily
Lachat - TKN	Lachat Manual	4 Conc. Glutamic Acid & Blank	Daily
Lachat - TP & TDP	Lachat Manual	4 Conc. KH <sub>2</sub> PO <sub>4</sub> & Blank	Daily
Lachat - NO <sub>2</sub> -NO <sub>3</sub>	Lachat Manual	4 Conc. KNO <sub>3</sub> , KNO <sub>2</sub> & Blank	Daily
Lachat - DRP	Lachat Manual	4 Conc. KH <sub>2</sub> PO <sub>4</sub> & Blank	Daily
Lachat - Cl	Lachat Manual	8 Conc. NaCl & Blank	Daily
Lachat - SiO <sub>2</sub>	Lachat Manual	8 Conc. Na <sub>2</sub> SO <sub>4</sub> & Blank	Daily
Technicon - DOC	Lachat Manual	4 Conc. Na <sub>2</sub> SiO <sub>3</sub> & Blank	Daily
Turner Dual Mono. Spectrofluorometer	Technicon Manual	Potassium Biphthalate	Daily
	Instrument Manual	Chlorophyll-a Chlorophyll b	Daily Daily

## ***7.0 Analytical Procedures***

The following are brief summaries of the analytical methods. Detailed methods for the following analytical procedures may be found in the WQS Field and Analytical Methods Manual.

### ***7.1 Physical Category Method Summaries***

#### **7.1.1 Turbidity**

Turbidity will be measured with a Turner Turbidimeter. The turbidimeter will be calibrated before analysis of each set of samples using a standard within the anticipated range of turbidity. All turbidity samples will be heated to 25°C to avoid condensation on the sample cuvet. Readings on the 0-1 range will be recorded to the nearest 0.01 unit and readings from 1-20 range will be recorded to the nearest 0.1 unit. These readings are accomplished after conductivity is determined. A portion of the conductivity sample is transferred to the cuvet for turbidity measurement since the sample is already at 25°C.

#### **7.1.2 Dissolved Oxygen**

Dissolved oxygen will be measured on water samples from all depths in Lake Erie and at the bottom depth in all other lakes, at each station on each survey. Analyses will be made by the azide modification of the Winkler test (EPA, 1974). The dissolved oxygen sample aliquot is obtained by inserting an 8 to 10 inch length of flexible plastic Tygon tubing connected to the Niskin bottle outlet plug to the bottom of a 60 ml glass BOD bottle. Flow will be regulated by the outlet plug so as to minimize turbulence and mixture of oxygen with the sample.

In addition, dissolved oxygen will be measured during the cast of the Sea Bird CTD with the built-in polarographic electrode.

#### **7.1.3 Specific Conductance**

Specific conductance will be determined using a YSI Model 35 conductivity bridge and a conductivity cell (YSI 3401 or YSE 3403,  $K = 1.0$ ). An immersion heater (such as is used for heating a cup of water for instant coffee), connected to a manually operated switch, will be used to heat the sample in a 250 ml polypropylene beaker to 25.0°C. The temperature will be monitored with a mercury thermometer (ASTM 90C) with 0.1°C divisions. Rapid stirring will be accomplished with an immersion glass paddle attached to a small electric motor. The apparatus will be standardized daily against a standard KCl solution according to the equation of Lind et al. (1959).

Conductivity will also be measured during the cast of the Sea Bird CTD. Raw conductivity measurements will be converted to specific conductance using empirically derived formulas.

#### **7.1.4 pH**

pH analyses will be made by electrometric measurement. pH meters will be standardized with pH 7.0 and 10.0 buffers, to bracket the pH of lake water. A combination Ross electrode with a platinum internal electrode element will be used. The pH measurement is taken by placing the pH probe in the water remaining in the conductivity sample (7.1.3) after the turbidity cuvet (7.1.1) has been filled. Measurements of pH will also be made during Sea Bird CTD casts.

### ***7.2 Nutrient Category Method Summaries***

#### **7.2.1 Total Alkalinity as $\text{CaCO}_3$**

Total alkalinity will be determined by titration to pH 4.5 with 0.02  $\text{NH}_2\text{SO}_4$ . The pH meter (Cole Parmer Model 5997), with Ross combination electrode, will be standardized daily with pH 4.0 and 7.0 buffers. The acid will be standardized against a standard  $\text{Na}_2\text{CO}_3$  solution.



### 7.2.2 Total Kjeldahl Nitrogen

Total Kjeldahl nitrogen samples will be preserved for no longer than 90 calendar days by the addition of 0.40 ml of  $\text{H}_2\text{SO}_4$  (310 ml/L) to each 125 ml. Preservative will be added to samples within 30 minutes of sample collection. Analyses will be made by an "ultramicro semiautomated" method (Jirka et al., 1976), in which a 10 ml sample is digested with a solution of  $\text{K}_2\text{SO}_4$  and  $\text{HgO}$  in a thermostated  $370^\circ\text{C}$  block digester. After cooling and dilution with water, the sample neutralization and ammonia determination (Berthelot Reaction) are accomplished on a Technicon Autoanalyzer System II.

### 7.2.3 Dissolved Nitrate and Nitrite Nitrogen

A Technicon Autoanalyzer will be used with Technicon's industrial method no. 158-71W (Armstrong et al., 1967; Grasshoff, 1969; FWPCA, 1969). In this procedure, nitrate is reduced to nitrite, in a copper cadmium column, which is then reacted with sulfanilamide and N-1-naphthylethylenediamine dihydrochloride to form a reddish purple azo dye. Nitrate and nitrite analyses will be performed within 48 hours of collection.

### 7.2.4 Total Phosphorus and Total Dissolved Phosphorus

Conversion of the various forms of phosphorus to orthophosphate is by an adaptation of the acid persulfate digestion method (Gales et al., 1966). Screw cap tubes containing samples and digestion solution will be heated in an autoclave at 15 psi ( $121^\circ\text{C}$ ) for 30 min. After cooling, the resulting orthophosphate is determined by the Technicon Autoanalyzer system II and Technicon's industrial method 155-71W (Murphy and Riley, 1962).

The sample storage bottle for total phosphorus will be agitated before sampling. Samples will be transferred to digestion tubes as soon as possible after sample collection.

### 7.2.5 Chloride

A Technicon Autoanalyzer System II will be used with Technicon's industrial method No. 99-70W (Zall et al., 1956; O'Brien, 1962). In this method chloride ion displaces mercury from mercuric thiocyanate forming unionized soluble mercuric chloride. The released thiocyanate reacts with ferric ion to form intensely colored ferric thiocyanate which is determined photometrically. Raw water samples, will be stored non-refrigerated in 125 ml or 250 ml polyethylene bottles with plastic closures.

### 7.2.6 Dissolved (Reactive) Silica

A Technicon Autoanalyzer System II is used with Technicon's industrial method No. 186-72W/Tentative (Technicon, 1973). This method is based on the chemical reduction of a silicomolybdate in acid solution to "molybdenum blue" by ascorbic acid. Oxalic acid is added to eliminate interference from phosphorus. Analyses will be performed on the filtered samples.

### 7.2.7 Dissolved Organic Carbon

Organic carbon will be determined on all filtered samples at all stations using a Technicon Autoanalyzer System II and Technicon's industrial method No. 451-76W. In this method, the acidified sample is purged with  $\text{CO}_2$ -free gas and then subjected to short wave UV radiation to convert carbon compounds to  $\text{CO}_2$ . The generated  $\text{CO}_2$  is measured with a nondispersive  $\text{CO}_2$  detector.

## 7.3 Microbiology Category Method Summaries

### 7.3.1 Chlorophyll "a" and Pheophytin

Samples for chlorophyll analysis (100 ml to 500 ml) will be taken from all depths at all stations and from the integrated or composite sample and will be filtered at  $<7''$  of Hg vacuum along with 1 to 2 ml of  $\text{MgCO}_3$  suspension (10 gm/l) usually within 30 minutes of sample collection. In some instances filtration may be delayed for as long as 2 hours. The filter (Gelman - Glass Fiber Filter type AE) will be retained in a capped glass tube containing 10 ml of 90% acetone at  $-10^\circ\text{C}$  in the dark for up to 30 days prior to completion of the analysis. The tubes will be treated in an ultrasonic bath for 20 minutes and then allowed to steep for a minimum of 24 hours prior to fluorometric analysis with a fluorometer (Strickland and Parsons, 1972).

In situ chlorophyll a measurements will also be made during Sea Bird casts.

### 7.3.2 Phytoplankton

Phytoplankton samples will be collected from all stations on the regularly scheduled cruises as well as at master stations on supplemental cruises. The samples will be representative of the upper 20 meters of the water column and will be collected as follows: whole water will be collected by Niskin bottle from 1, 5, 10, and 20 meters.

Approximately 960 ml of sample from each depth (1, 5, 10, and 20 meters) will be mixed in a one-gallon cubitainer. Approximately 960 ml of the mixed sample will be transferred to a 960 ml bottle and immediately preserved with 10 ml of modified Lugol's solution for phytoplankton analysis. The remaining volume in the cubitainer will be designated the "Integrated Sample" and will be used for chemical analysis.

At CRL diatoms will be cleaned with 30%  $\text{H}_2\text{O}_2$  plus  $\text{K}_2\text{Cr}_2\text{O}_7$  and mounted in Hydrax. At least 500 frustules per sample will be enumerated and identified at 1250X. Other algal forms will be identified and enumerated at 500X using a modification of the Utermohl (1958) method.

Biovolumes will be determined for each sample by assigning an appropriate geometric shape and making the necessary measurement for the volume calculation. A minimum of 10 individuals of each common species will be measured in each sample. Less common organisms will be measured when they occur.

### 7.3.3 Zooplankton

Samples for crustacean zooplankton will be collected by vertical tow. Zooplankton tows will be made from B-2 meters to the surface and from 20 m to the surface at each station using a 62 micron mesh plankton net with a 0.5 meter mouth opening. At master stations, duplicate tows will be taken for evaluation of the representativeness of the tows collection of the zooplankton assemblages volume of water sampled for each tow will be determined by recording the before and after tow reading of a flow meter mounted in the mouth of the plankton net.

Following collection, the plankton net shall be hosed down (from the outside only!) to wash organisms adhering to the side of the net into the collection cup. The contents of the cup shall be rinsed twice with distilled or potable water and the washings added to the sample bottle. Ten to fifteen ml of the narcotizing agent (club soda) shall be added to each sample.

The bottle shall be inverted two or three times to assure mixing and then allowed to stand 10 or 20 minutes for narcotization to take effect. Samples will then be preserved with 5% formalin (10 ml concentrated formalin/250 ml sample). Each sample will be labeled with the regular station number and the depth at which the tow was begun. An entry will be made on the zooplankton field sheet indicating station number, date time, depth at which the tow was begun and the before and after tow flow meter reading, as well as wire angle during the tow.

### 7.3.4 Primary Productivity Parameters

Samples for analysis of primary productivity will be collected at selected sites in parallel with those for phytoplankton enumeration: during the summer survey a separate sample from the M3 depth will be taken for analysis also. Approximately 4L of composited water sample will be collected into a darkened carboy or cubitainer, and the carboy placed immediately in a light-tight insulated chest for transportation to the shipboard laboratory. The water sample will be transferred to 300 ml incubation bottles and inoculated with a known quantity of bicarbonate substrate which is labeled with the radiotracer  $C^{14}$ . Samples from the same water source are incubated at temperatures approximating ambient, at various light intensities for 2 to 4 hours, after which the algal cells are separated from the water by filtration.

The filters are immersed in a scintillation cocktail and returned to CRL for counting in a liquid scintillation counter. Because the measured radio activity of each filter will be proportional to the quantity of carbon fixed by the algae into organic material, the metabolic activity of the algae community can be established.

Calculation of the productivity parameters also require information about the total inorganic carbon available in the incubation vessel, the length of time of incubation, the chlorophyll content of the incubated sample and the specific activity of the radiotracer.

#### 7.4 Analysis Priority Ranking

If it appears that onboard holding time goals will not be reached, the ASCL Chemistry Supervisor and the EPA Survey Supervisor will be notified. The EPA Survey Supervisor will assign priority to backlog analysis. Suggested prioritizations are listed in Table 7-1. Sample collection will be interrupted until the backlog is reduced so that on board holding times are met.

Suggested order of biological analysis is:

- 1) productivity
- 2) chlorophyll
- 3) DAPI, sample preservation

**Table 7-1. Prioritization and Preservation of Chemistry Samples**

PRIORITY	PARAMETER	OPERATIONAL MAXIMUM HOLDING TIME	PRESERVATIVE/ STORAGE	COMMENTS
1	physical tests, turbidity, DO, Cond., pH, alk., All filtration	Perform ASAP	None	Unstable
2	SRP	48 hr.	4° C/Iced	Unstable
3	NO <sub>2</sub> + NO <sub>3</sub>	48 hr.	4° C/Iced	TKN samples may be used but AVOID CONTAMINATION
3	TDP, DOC	48 hr.	4° C/Iced	Filter immediately
4	TP	48 hr.	1 ml H <sub>2</sub> SO <sub>4</sub> /L	TKN samples may be used
5	POC, TKN	Analyzed at CRL	Analyzed at CRL	Analyzed at CRL

\*When these samples are returned to the CRL, they will be analyzed within 90 days of the collection date.

Within these restrictions, backlogged samples will be analyzed on the Guardian on a "first-in-first-out" schedule.

## ***8.0 DATA REDUCTION, VALIDATION & REPORTING***

The flow of data for the LMMB SURVEY is depicted in Figure 8.1. Details of the various activities identified on the flowchart are discussed in Appendix B and below.

**Figure 8.1 LMMB SURVEY data flow**

### ***8.1 Calculations and Units***

All calculations used to reduce raw data to its final form are presented in each analytical method. Units are also specified for each method and in Table 1-2.

### ***8.2 Raw Data***

All shipboard generated strip charts, bench records, and computer printouts will be kept in a folder, indexed by station, until the remaining samples (e.g., Metals, TKNs and reruns) are transferred to the CRL. A master folder will be prepared to hold all sample information and additional data as it is generated, reviewed and approved. All raw data will be assembled and indexed by parameter by lake and by survey leg. Analogue charts and digital conversion printouts will be stapled together. Each parameter will be put in a manilla folder and given to GLNPO.

### 8.3 Data Verification

The intent of this subsection is to describe the various mechanisms that are used in defining and implementing the data verification procedures and the corrective actions that are taken if the MQOs are not satisfied. All data generated will go through the same review process required in the Contractors QA Project Plan. Figure 8.2 provides a flowchart of the data review process required by the Contractor. No data, whether generated on board or in the laboratory will be released to GLNPO without this review. The following information provides specific activities for the data verification of the three LMMB SURVEY Categories.

#### 8.3.1 Nutrient Category

Verification of Nutrient Category parameters is accomplished primarily through the application of a data verification template. Figure 8.3 is an example of a data verification template for the LMMB SURVEY Nitrate/Nitrite parameter. Appendix C contains the remainder of the templates. The templates provide an assessment checklist of QE/QC samples for each analytical batch. The templates are used to make decisions on whether to request reanalysis for a particular parameter and are designed to assess data on the basis of the MQO requirements.

The templates are constructed as spreadsheets, where the row entry fields specify the evaluation criteria and the column entry fields represent the magnitude of the measurement uncertainty that has occurred. The first column is used to identify major measurement uncertainty and the second column identifies minor uncertainty. When uncertainty occurs, the QA manager informs the laboratory manager to check for errors in the data for the suspect run and parameter before initiating reanalysis. If the laboratory confirms the values, then reanalysis may be requested for all samples in the batch.

The contract laboratory generally operates as follows: (1) perform analysis; (2) enter results into **RLIMS**; (3) review data and correct errors, if necessary; (4) perform and evaluate verification checks; (5) reanalyze if necessary (repeat previous steps); (6) select appropriate run for submission if reanalysis is performed; (7) submit data to QA staff. This process is repeated for each parameter until the entire batch is complete for all parameters and ready for formal submission.

Analyst
1) conduct analysis
2) determine if QC meets limits
3) initiate corrective action if needed
4) initial data
Contractor's Team Chief
1) review QC results
2) check appropriateness & effectiveness of corrective action
3) review data for completeness

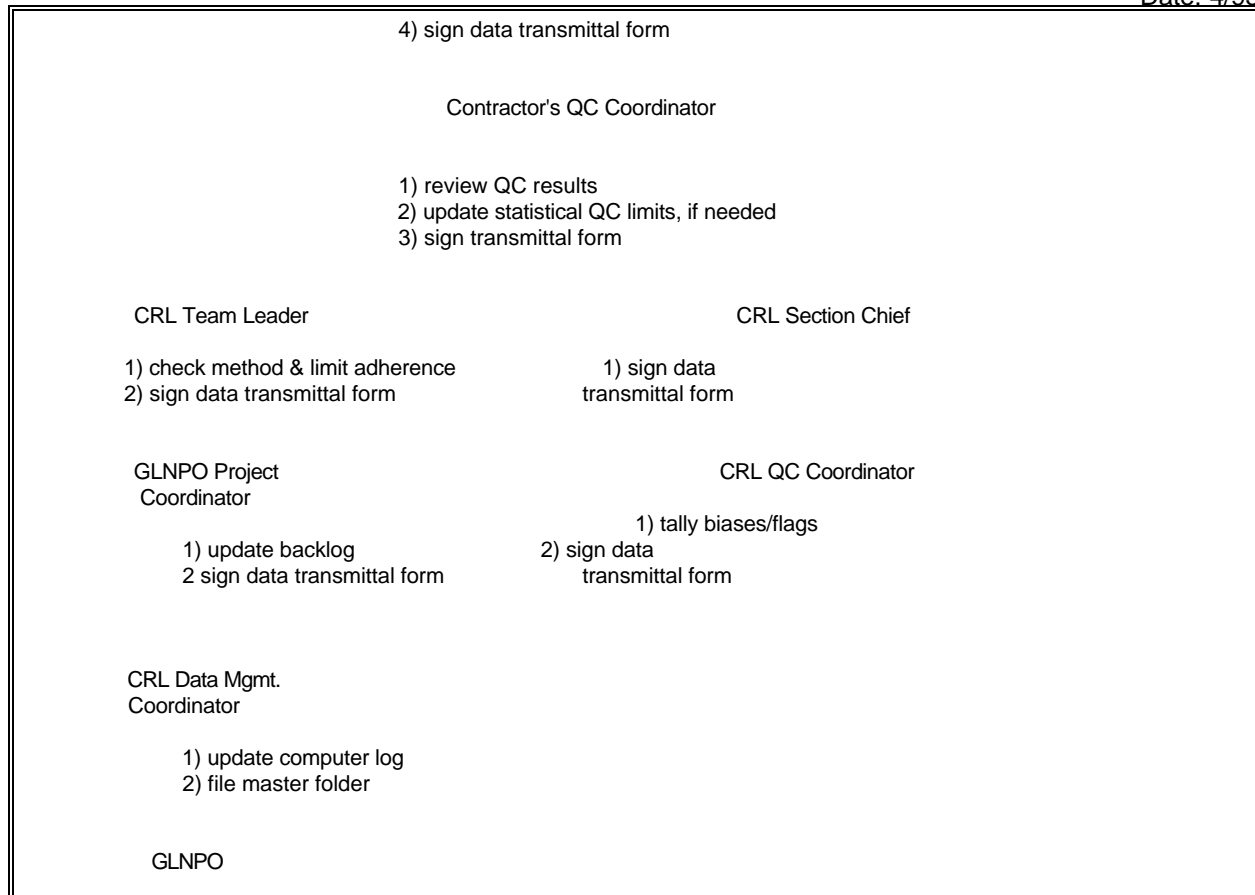


Figure 8.2 Data and QC review flowchart

### 8.3.2 Physical Parameters

### 8.3.3 Biological Parameters

Measurement	Measurements Quality Samples	Major Reanalysis if non-compliance in two or more categories	Minor Reanalysis if non-compliance in three more categories
LPC-1		If <b>one</b> relationship occurs: 1) $\bar{A} > 0.03$ 2) mean $< 0.08$ or $> 0.12$	If <b>one</b> relationship occurs: 1) $\bar{A} > 0.03$ 2) mean $< 0.08$ or $> 0.12$
LPC-2		If <b>one</b> relationship occurs: 1) RPD $> 20$ 2) mean $< 0.37$ or $> 0.43$	If <b>one</b> relationship occurs: 1) RPD $> 20$ 2) mean $< 0.37$ or $> 0.43$
FD1		None	$\bar{A} < 0.15$ if mean $< 0.37$ or RPD $< 40$ if mean $> 0.37$
FS1		$\bar{A} > 0.10$ if mean $< 0.33$ or RPD $> 30$ if mean $> 0.33$	$\bar{A} > 0.10$ if mean $< 0.33$ or RPD $> 30$ if mean $> 0.33$
LS1		$\bar{A} > 0.03$ if mean $< 0.15$ or RPD $> 20$ if mean $> 0.15$	$\bar{A} > 0.03$ if mean $< 0.15$ or RPD $> 20$ if mean $> 0.15$
LR1		If <b>both</b> relationship occurs: 1) Mean within accuracy windows 2) $\bar{A} > 0.03$ if mean $< 0.15$ or RPD $> 20$ if mean $> 0.15$	If <b>one</b> relationship occurs: 1) Mean within accuracy windows 2) $\bar{A} > 0.03$ if mean $< 0.15$ or RPD $> 20$ if mean $> 0.15$
LRB		Value $> \text{RMDL}$	Value $> \text{RMDL}$
LCB		Value $> \text{RMDL}$	Value $> \text{RMDL}$
FRB		None	Value $> 2^* \text{RMDL}$

Figure 8.3. Verification Template for the LMMB SURVEY Nitrate/Nitrite Analysis

#### 8.4 Out of Control Criteria

All QC audit results falling outside the statistically established control limits (see method or Table 3-1) are outliers. Outliers must be flagged. The flag codes are listed in Appendix D. The analytical system should not generate data on any real samples until it has been determined whether the outlier is a normal low probability result or the measurement system is out of control. If the outlier is a simply a low probability result in an otherwise properly operating system, then the samples and QC audit results should be retained. If the system is out of control, the system brought into a properly operating mode prior to rerunning the subject samples. If samples can not be reanalyzed, the data will be flagged accordingly and during validation procedures, may eventually be removed from the data base.

#### 8.5 Data Validation

Data validation is the final process of determining what data will be used to answer the programs objectives. Through the review of data flags, field and laboratory logbooks and other information pertaining to the data, the data is determined to be "useable" for the project. These validation procedures will be documented in the final reports.

#### 8.6 Computer Support

User documentation for A/D transfer of data and down loading of concentrations is found in Appendix E.

#### 8.7 Reports

Annual statistical reports of aggregated data are anticipated. Within these reports, a QA section which determines the quality of the data reported will also be included. Topics in this section will include:

- Overall quality with respect to the DQOs.

- Adherence to MQOs.

- Statistical evaluations of precision, accuracy, completeness, and detectability.

- Review of technical systems audits.

- Lessons learned and proposed revision to the QA Project Plan.

- Performance evaluations and laboratory comparison studies.



## 9.0 Internal QC Procedures

Internal QC procedures are used to control measurement uncertainty in real time. This is accomplished through the use of various QC samples that allow one to determine if the measurement system is in control. The type, frequency and acceptance criteria for all QC samples are found in Tables 3-1, 3-2 and 3-3. Calibration standards can be found in the SOPs. Definitions of these samples are presented in Section 3. Brief discussions of the three parameter categories are presented.

### 9.1 Nutrient Category

Figure 3.1 identifies the internal QC samples for the nutrient category. Although the FS1/LS1 split samples are identified on the "QE sample" side, since they are split in the laboratory, they are considered internal QC samples. The contract laboratory is aware of the MQOs for these samples. A verification template has been developed for these internal QC samples as illustrated in Figure 9.1. In the case of the contract laboratory internal QC template, there is no major and minor criteria as was illustrated Figure 8.3. In this case, if any two categories (2 out of 5) fail the criteria, corrective action is taken. Corrective action would be in the form of 1) confirming the values are correct (no entry errors etc.), and 2) reanalyses of the batch for the particular parameter.

Parameter	LPC-1 If <b>one</b> relationship occurs:	LPC-2 If <b>one</b> relationship occurs:	LRB	LCB	FS1/LS1
Total Kjeldahl N	1) LPC-1 Pair $\bar{A} > 0.05$ 2) LPC-1 pair mean $< \_\_\_$ or $> \_\_\_$	1) LPC-2 Pair RPD $> 20$ 2) LPC-2 pair mean $< \_\_\_$ or $> \_\_\_$	$< \_\_\_$ or $> 0.05$	$< \_\_\_$ or $> 0.05$	$\bar{A} > 0.05$ if mean $< 0.25$ or RPD $> 20$ if mean $> 0.25$
Nitrate + Nitrite N	1) LPC-1 Pair $\bar{A} > 0.03$ 2) LPC-1 pair mean $< 0.08$ or $> 0.12$	1) LPC-2 Pair RPD $> \_\_\_$ 2) LPC-2 pair mean $< 0.37$ or $> 0.43$	$< \_\_\_$ or $> 0.03$	$< \_\_\_$ or $> 0.03$	$\bar{A} > 0.03$ if mean $< 0.15$ or RPD $> 20$ if mean $> 0.15$
Total P	1) LPC-1 Pair $\bar{A} > 0.002$ 2) LPC-1 pair mean $< \_\_\_$ or $> \_\_\_$	1) LPC-2 Pair RPD $> 10$ 2) LPC-2 pair mean $< \_\_\_$ or $> \_\_\_$	$< \_\_\_$ or $> 0.002$	$< \_\_\_$ or $> 0.002$	$\bar{A} > 0.002$ if mean $< 0.02$ or RPD $> 10$ if mean $> 0.02$
Total Dissolved P	1) LPC-1 Pair $\bar{A} > 0.002$ 2) LPC-1 pair mean $< \_\_\_$ or $> \_\_\_$	1) LPC-2 Pair RPD $> 10$ 2) LPC-2 pair mean $< \_\_\_$ or $> \_\_\_$	$< \_\_\_$ or $> 0.002$	$< \_\_\_$ or $> 0.002$	$\bar{A} > 0.002$ if mean $< 0.02$ or RPD $> 10$ if mean $> 0.02$
Chloride	1) LPC-1 Pair $\bar{A} > 0.2$ 2) LPC-1 pair mean $< \_\_\_$ or $> \_\_\_$	1) LPC-2 Pair RPD $> 10$ 2) LPC-2 pair mean $< \_\_\_$ or $> \_\_\_$	$< \_\_\_$ or $> 0.2$	$< \_\_\_$ or $> 0.2$	$\bar{A} > 0.2$ if mean $< 2.0$ or RPD $> 10$ if mean $> 2.0$
Total Suspended Solids	1) LPC-1 Pair $\bar{A} > 0.54$ 2) LPC-1 pair mean $< \_\_\_$ or $> \_\_\_$	1) LPC-2 Pair RPD $> 15$ 2) LPC-2 pair mean $< \_\_\_$ or $> \_\_\_$	$< \_\_\_$ or $> 0.54$	$< \_\_\_$ or $> 0.54$	$\bar{A} > 0.54$ if mean $< 3.6$ or RPD $> 15$ if mean $> 3.6$
Reactive Si	1) LPC-1 Pair $\bar{A} > 0.015$ 2) LPC-1 pair	1) LPC-2 Pair RPD $> 15$ 2) LPC-2 pair	$< \_\_\_$ or $> 0.015$	$< \_\_\_$ or $> 0.015$	$\bar{A} > 0.015$ if mean $< 0.1$ or

	mean < ____ or > ____	mean < ____ or > ____			RPD > 15 if mean > 0.1
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**Figure 9.1 Nutrient Category internal QC verification template.**

## **9.2 Physical Category**

In this category, internal QC is method dependent (on a parameter by parameter basis) since some measurements are recorded directly from instrumentation or observation while others undergo some preparation and analysis.

## **9.3 Biological Category**

### **9.4 Recording and plotting of QC data**

Analysts will make every attempt to make maximum effective use of QC data. Specific steps toward this end include prompt entry of the QC results in the QC data base and plotting that data on the appropriate control charts.

Prior to the survey, the lab contractor's QC Coordinator will be responsible for assuring that the system logs are available and current. He/she will assure that the control charts, covering all internal QC checks are available with the proper limits (MQOs).

Each QC check will have at least one control chart constructed. The control chart will be updated after each batch and will be used to determine trends in the analyses process. Each analyst will maintain the logs and control charts for their assigned parameters on an ongoing basis. Each analyst will regularly evaluate whether the analytical system is in control. Each analyst will report actual or suspected impending out-of-control situations to the contractor shift supervisor. Corrective action for beyond-limit situations are discussed in section 13.0. Charts are to include the date the point was generated, the associated station number and notations of extraordinary situations. Entries should be made to indicate the preparation of new batches of control standards and calibration standards.

## **10.0 Performance and Systems Audits**

An audit or assessment is a formal evaluation of performance to pre-determined standards and the evaluation and documentation to effect change towards improved performance. Audits are the principal means used by EPA to determine compliance and to control systems in a real-time manner to improve performance. EPA defines and uses four types of audits: 1) technical systems audits (TSAs), 2) data quality assessments (DQAs), 3) management systems reviews (MSRs), and 4) performance evaluations (PEs). These assessments will be utilized in the LMMB SURVEY.

### **10.1 Technical Systems Audits (TSAs)**

Technical systems audits (TSAs) are qualitative on-site evaluations of a complete phase of an EDCA (i.e., sampling, preparation, analysis). This audit can be performed prior to the data collection activity, in order to verify the existence and evaluate the adequacy of equipment, facilities, supplies, personnel, and procedures that have been documented in the QAPjP. TSAs are also employed during the data collection activity in order to verify and evaluate the EDCA.

A TSA will be performed once a year for the field and analytical activities of the LMMB SURVEY. The QAM will schedule field audits with the GLNPO Survey Supervisor and laboratory audits with the EPA Project Officer. The QAM will assist in planning the audit as discussed in section 10.5. However, the GLNPO Survey Supervisor and the EPA Project Officer are responsible for developing an audit plan (Section 10.5) and documenting audit results (Section 10.6).

### **10.2 Data Quality Assessments (DQAs)**

A data quality assessment (DQA) focuses on collected data. It is used to determine if enough QA information exists with the data set to evaluate the quality of the data and whether this quality satisfies the stated DQOs of the EDCA. It is also used to assess the ability of the QAPjP to produce data of known and satisfactory quality.

DQAs will be a part of the reporting requirements as discussed in Section 8. In some instances a major QA report may be written for information on a larger aggregate of data (i.e, for the LMMB SURVEY data base) in which a more rigorous DQA will be implemented.

### **10.3 Management Systems Reviews (MSRs)**

A management systems review (MSR) is an on-site evaluation by the organizations senior management to assess the organizations internal management structure and its documents to determine whether the organization is implementing a satisfactory QA program. It is used to determine the effectiveness of, and adherence to the QA program and the adequacy of resources and personnel provided to achieve and ensure quality in all activities.

The MSR includes reviews of:

- Procedures for developing DQOs.
- Procedures for developing and approving QA Project Plans (QAPjPs).
- The quality of existing QAPjP guidance and QAPjPs.
- Procedures for developing and approving standard operating procedures (SOPs).
- Procedures and criteria for designing and conducting audits.
- Tracking systems for assuring that the QA program is operating, and that corrective actions disclosed by audits have been taken.

The degree of management support.

Responsibilities and authorities of the various line managers and the quality assurance program manager for carrying out the QA program.

An MSR of the LMMB SURVEY QA program will be conducted at a minimum of once every three years; more frequently if serious deficiencies exist. The review should occur between the months of October and February, before implementation of sampling activities, and to allow results to be utilized in the next survey.

In order to achieve the MSRs objectives, the review should be lead by the GLNPO Directors Office or an independent agency with QA experience (QAMS). The lead could then choose a review team from GLNPO senior management who would assist in the planning, scheduling, and implementing the review. The review team would determine the scope of the review which would include reviews of the bullets mentioned above. An audit plan, as discussed in section 10.5 will be developed.

The team will present their findings in a report directed to GLNPO management. Action items on any deficiencies will be developed and discussed in this report and will become goals for improvement. Review of progress on actions items will be discussed at management and staff meetings.

#### **10.4 Performance Evaluations (PEs)**

Performance evaluations (PEs) are a means of independently verifying and evaluating the quality of data from a measurement phase, or the overall measurement system. This is accomplished through the use of samples of known composition and concentration. These samples can be introduced into the measurement system as single blind (identity is known but concentration is not) or double blind (concentration and identity unknown). These samples can be used to control and evaluate accuracy and precision and to determine whether DQOs or MQOs have been satisfied. PEs can also be used to determine inter- and intra-laboratory variability and temporal variability over long projects, and to evaluate laboratories prior to contract awards.

Figure 3.1 illustrates the use of PEs in the LMMB SURVEY Nutrient Category. The contract laboratory also participates in round-robin analyses which is facilitated by the Canadian National Water Research Institute. Data from PEs and round-robin studies will be documented in the QA section of the LMMB SURVEY data reports.

#### **10.5 Audit Plan**

Audit planning is a necessity in order to conduct efficient audits. An audit plan for LMMB SURVEY audits will include the following items:

Audit title.

Audit number - Year and number of audit can be combined; 93-1, 93-2

Date of audit.

Scope - Establishes the boundary of the audit and identifies the groups and activities to be evaluated. The scope can vary from general overview, total system, to part of system, which will effect the length of the audit.

Purpose - What the audit should achieve.

Standards - Standards are criteria against which performance is evaluated. These standards must be clear and concise and should be used consistently when auditing similar facilities or procedures. The use of audit checklists is suggested to assure that the full scope of an audit is covered.

Audit team - Team lead and members.

Auditees - People that should be available for the audit from the audited organization. This should include the Program Manager, Principal Investigator, organizations QA Representative, and other management, and technicians as necessary.

Documents - Documents that should be available in order for the audit to proceed efficiently. Too often documents are asked for during an audit, when auditors do not have the time to wait for these documents to be found. Documents could include QMPs, QAPjPs, SOPs, GLPs, control charts, raw

data, QE/QC data, previous audit reports etc.

Timeline - A timeline of when organizations (auditors/auditees) will be notified of the audit in order for efficient scheduling and full participation of all parties.

### **10.6 Audit Reporting**

A debriefing will occur at the completion of the audit. Positive and negative aspects of the EDCA will be discussed between the audit team, management of the area audited, and, if necessary, technical personnel performing the measurement activity. Copies of the draft audit summary and findings should be provided to all those in attendance. Necessary action to improve the measurement system will be discussed with project participants.

In the case of TSA, DQAs and PEs, the responsibility for reporting rests with the Project Officer or the Survey Supervisor, though he/she may not be the review team lead for the audit. Responsibility for reporting MSRs is the responsibility of the review team lead or an appointed designee. The report will include:

- Audit title and number and any other identifying information.

- Audit team leaders, audit team participants and audited participants.

- Background information about the project, purpose of the audit, dates of the audit, particular measurement phase or parameters that were audited, and a brief description of the audit process.

- Summary and conclusions of the audit and corrective action requires.

- Attachments or appendices that include all audit evaluation forms and audit finding forms.

The audit finding form can be found in Appendix F. The report will be completed within five working days of completion of the audit. TSA, DQA, and PE reports will be reviewed, signed by the QAM and Project Officer, and filed with the QAM. MSR reports will be reviewed, signed by the audit lead and the GLNPO Director and filed in the Directors office and by the QAM. It is the responsibility of the review team lead to forward audit reports to the appropriate project participants. The audit report has restricted distribution in order to foster constructive working relationships. When significant concerns are identified on audit finding forms, a meeting will be scheduled with the appropriate parties.

### **10.7 Response Actions**

The audit reports will be discussed with the audited organization and action necessary to rectify and control the situation will be developed. Line management may be requested to assist in problem resolution as necessary. For each audit finding form, an audit finding response form (Appendix F) will be developed to track corrective actions. This information will be included in the audit file retained by the QAM. The Project Officer (TSAs, DQAs PEs) or the GLNPO Director (MSRs) are responsible to ensure compliance with the corrective actions. If major deficiencies are found, follow-up audits may be required and should be discussed.

## **11.0 Preventative Maintenance**

Preventative maintenance is necessary to keep analytical instruments and other equipment in good working condition and to decrease the amount of major repairs and downtime. Most analytical instrument and equipment manuals have a section dealing with preventive maintenance. These sections will be read by each person operating the equipment. All preventative maintenance performed will be noted in the system logbook.

The use of QC samples and the calibration requirements for the survey parameters (Table 6-1) can be used as an indicator of necessary equipment maintenance. Instruments requiring calibration above normal frequency will be identified and evaluated for maintenance.

After each survey, all on board instruments will be inspected for worn parts or erratic behavior as indicated by QC results. The inspection will be recorded in the system logbook for each instrument.

An on board back up recorder, sampler, colorimeter, pump, manifold, tubing supply and small replacement parts will be kept. The Contractor Survey coordinator will maintain an inventory of this equipment. Each SOP contains an equipment list. Enough equipment will be on hand, especially for field sampling conditions, for replacement to reduce "down time". The contractor will maintain a list of all frequently used items including the current vendor and catalog number.

To prevent equipment misuses, the lab Contractor will assure that its employees follow all operational procedures for each instrument utilized. This assurance is maintained by the development of detailed SOPs, training/certification, and "dry run" activities discussed in Section 4.

The lab Contractor will maintain the system logbooks on each instrument used. All calibration procedures performed on the instrument and a record of all maintenance performed will be documented. The Contractor's Project Manager or the QC Coordinator will inspect these logbooks after each survey to determine the instrument's condition and performance. Any failure/breakdowns will be reported immediately to both the Contractor's Project Manager and the EPA Project Officer. This action will be the responsibility of the individual operating the instrument when such an event occurs.

The lab Contractor will operate within all established CRL Quality Assurance procedures for equipment, glassware and reagents. Parts that need periodic replacement will be requested at a rate to ensure that parts are always on hand.

The lab Contractor will have at least one employee attend each CRL Safety Meeting to ensure that all safety concerns are addressed promptly.

## 12.0 Calculation of Data Quality Indicators

This QA Plan has defined the DQOs and MQOs (Section 3). This section describes the statistical assessment procedures that are applied to the data and the general assessment of the data quality accomplishments.

### 12.1 Precision

The precision will be evaluated by performing duplicate analyses. Various types of duplicate samples are described in Section 3. Precision will be assessed by the following three methods:

#### 1) Difference

$$\text{Difference} = X_1 - X_2$$

Where:  $X_1$  = larger of the two observed values  
 $X_2$  = smaller of the two observed values

This formula is used for parameters with concentrations below some established value (knot) or in all cases such as pH or many of the direct observation parameters in the physical category.

#### 2) Relative Percent Difference (RPD)

This formula is used for duplicate measurements above some defined concentration (knot).

#### 3) Relative Standard Deviation (RSD)

Where:  $s$  = standard deviation  
 $y$  = mean of replicate analyses

This formula is used for three or more replicate values and may be used when reporting precision on aggregated data.

Standard deviation is defined as follows:

Where:  $y_i$  = measured value of the  $i$ th replicate  
 $y$  = mean of replicate analyses  
 $n$  = number of replicates

In expressing overall variance of the measurement system, as described in Section 3, pooled data from field duplicates (FD1) will be used. Since field duplicates are routine samples in which the actual concentration is unknown, the estimate of overall variance may be influenced by concentration. The influence of concentration on variance will be evaluated and the most appropriate approach to estimating overall variance will be developed.

### 12.2 Accuracy

Accuracy will be based upon PE samples of "known" concentration that are either known or blind to the laboratory. Field and laboratory blank samples can also be used in the assessment of accuracy.

Accuracy will be evaluated by determining whether the concentration of the PE samples are within the required acceptance windows. These windows have been either established by the vendor supplying the

PE material, whereby a certificate of analyses is included, or through the use of this sample by many laboratories using the same or a similar method, thereby establishing an accepted window. Deviations beyond the acceptance windows could be justification for reanalyses.

The PE samples, especially the mid-range check sample (FR1) for the Nutrient Category can be used to assess accuracy from a system-wide measurement perspective. Bias will be estimated from the theoretical PE value. Bias for a particular PE sample is defined:

Where:  $Y_{ik}$  = the average observed value for the  $i$ th audit sample and  $k$  observations.  
 $R_i$  = is the theoretical reference value  
 $n$  = the number of reference samples used in the assessment

If it is determined that bias is independent of concentration, then this equation could be used as an estimate of system bias. The influence of concentration on bias will be evaluated and the most appropriate approach to estimating overall bias will be developed.

### 12.3 Completeness

Completeness for most analyses should be 95% since the samples are available for reanalysis in the event that the analytical procedure goes out of control for some reason. Completeness is defined:

Where:  $V$  = number of samples judged valid  
 $n$  = total number of measurements necessary to achieve project objectives

The 95% goal means that the objectives of the survey can be met, even if 5% of the samples are deemed to be invalid. An invalid sample is defined by a number or combination of flags associated with the sample. This value will be reported on an annual basis.

### 12.4 Representativeness

Based upon the objectives, the two yearly lake surveys (spring and summer) represent different lake conditions; the spring survey, which measures initial conditions and provides a consistent estimate of change from year to year, while the summer survey attempts to measure condition during a biologically active period. Change would be determined by evaluating a number of spring surveys or a number of summer surveys. In order to determine whether a change is statistically significant, the samples must be representative of the population from year to year and the samples must be collected and analyzed in a consistent manner.

Each lake is considered a population and change is reported on a lake by lake basis. The number of sites have been selected in order to meet the objectives. Methods for sampling and analyses have not changed significantly to influence the evaluation of data.

Representativeness will be evaluated through variance estimates of routine sample in comparison to previous years estimates. These estimates can be performed at within-site and between-site levels. Analysis of variance (ANOVA) will be used to determine whether variances are significantly different.

### 12.5 Comparability

Comparability is very similar to representativeness in that comparability is ensured through the use of similar sampling and analytical techniques. Comparability will be assessed through the evaluation of precision and accuracy estimates of QA/QC samples within and between years.



## 12.6 Detectability

An important factor to consider in data quality evaluations is the detection limit, which is defined as the lowest value of a characteristic that a measurement process, or a method-specific procedure can reliably discern. Table 1-2 identifies the required method detection limits (RMDLs) for the LMMB SURVEY parameters. The procedure for determining the MDL is defined in 40 CFR Pt. 136, APP.B. However data from various QC samples (FRB) can be pooled to provide estimates of overall detectability defined as the system detection limit (SDL) and for specific instruments defined as instrument detection limits (IDL).

Detection limits in general are defined:

$$\text{Detection Limit} = t_{(n-1, 1-\alpha=0.99)} * s$$

Where:

$t_{(n-1, 1-\alpha=0.99)}$  = student's t-value for a one sided 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

s= standard deviation

### **13.0 Corrective Action**

In general, this QAPjP has been written to minimize the need for corrective action. However, the purpose of the QAPjP is also to quickly identify a problem and to correct the problem prior to any serious effect on the integrity of the project results.

Corrective action will be identified by:

- Identification of problems by samplers/analysts
- Technical systems audits
- QA/QC sample evaluation
- Laboratory comparison studies

These activities are all a part of the LMMB SURVEY and specific corrective action techniques have been discussed in sections 8, 9 and 10.

Any indication that a system is out of control will be brought immediately to the attention of the Contractor's shift supervisor. Regardless of the course of action, there are three possibilities:

- 1) The procedure is declared to have been in control, in which case the original data results are accepted.
- 2) The procedure is determined to be out of control, in which case, modifications are made to correct the situation, the original data is flagged along with an explanation of the problem and its resolution. The original samples are then rerun and if acceptable, the new results of the routine and QE/QC samples replace the original data. Only then is the original data replaced and must be determined by the EPA Project Officer in conjunction with the EPA principle investigator.
- 3) If it is inconclusive whether the system was in control or not, but it is operating properly at the present, then continue as in 2 above. If data does not change significantly, the principle investigator, in consultation with the analysts decide which analytical run to accept.

Feedback to the employees and suggestions for corrective actions will be the supervisor's responsibility. In the event that the only way that a procedure can be brought under control is by a procedure modification, this must be reported to the Contractors QC Coordinator, Contractor's Survey Supervisor, the GLNPO Survey Supervisor and the EPA Project Officer. Documentation will be in the form of a written variance to the establish procedure. Written documentation will be presented to, Contractor's Project Officer and to EPA's Survey Supervisor and Project Officer.

Contractor's Survey Coordinator and EPA's Survey Supervisor can stop analysis if a measurement system cannot be brought under control.

If a back log of samples develops such that it can not be cleared within the holding time limits if additional samples are taken, then the collection of samples will be interrupted until the back log is cleared. The recommendation to halt sampling will be made by Contractor's Survey Supervisor. The decision to stop sampling will be made by EPA's Survey Supervisor.

APPENDIX A

TABLE 1

SHIP SCHEDULE 1994

DATE	ACTIVITY / LOCATION	TYPE OF SHIP DAY
April 22	St. Ignace Mi. Transit to L.M.	
	Extended Travel	
Spring Survey - Lake Michigan		
April 23-30	Sampling Lake Michigan	Extended Operations
May 01-11	Sampling Lake Michigan	Extended Operations
First Air Intensive Lake Michigan		
May 12-14	Milwaukee Wi. Prep Air Work	Extended Travel
May 15-21	Air Monitoring L. Michigan	Extended Operations
May 22	Remove Methylene Chloride Ludington	Extended Travel
May 23	Remove Waste Chemicals Milwaukee Wi	Extended Travel
Monitoring Survey - Lake Michigan		
June 11	Chemical Waste Removal (if needed)	Extended Travel
June 12	Prep for Mass Balance Survey	Extended Travel
June 13-30	Sampling Lake Michigan	Extended Operations
July 01-09	Sampling Lake Michigan	Extended Operations
Second Air Intensive - Lake Michigan		
July 10-16	Milwaukee Wi-Prep Air Survey	Extended Travel
July 17-31	Air Monitoring L. Michigan	Extended Operations
Summer Monitoring - Lake Michigan		
August 01	Prep for Mass Balance Survey	Extended Travel
Aug 02-15	Sampling Lake Michigan	Extended Operations
Aug 16-17	St. Ignace/Mackinaw Island	Extended Travel
Aug 18-24	Sampling Lake Michigan	Extended Operations
August 25	Chemical Waste Removal	Extended Travel
Third Air Intensive - Lake Michigan		
Oct 29	Chemical Waste Removal Milwaukee Wi	Extended Travel
Oct 30	Preparation Air Monitoring L.Mich	Extended Travel
Nov 01-14	Air Monitoring Lake Michigan	Extended Operations
Nov 15	Chemical Waste Removal Milwaukee Wi	Extended Travel